MODELLING OF LOW TEMPERATURE OXIDATION OF COAL DUMPS

Rufaro Kaitano

A dissertation submitted to the Faculty of Engineering, University of the Witwatersrand, Johannesburg, for the Degree of Master of Science.

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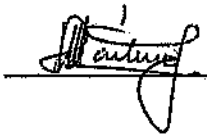
DECLARATION

I declare that this dissertation is my own unaided work, and has not been submitted before for any degree or examination in any other University.

signature  .

25th day of September 1998

ABSTRACT

Storage and waste dumps from coal mining tend to spontaneously combust. This is mainly as a result of the oxidation process which is accelerated by the availability of oxygen and the exothermic nature of the oxidation process. In cases of poor ventilation the heat accumulation within the bed is thought to lead to the spontaneous combustion of coal.

The work in this dissertation aims to investigate the change in oxygen concentration in a bed of coal and also measure the rate of oxidation (oxygen absorption) in a closed reactor under isothermal conditions. Drying rate of coal under nitrogen was also looked into.

An analysis of the oxygen concentration profile in a three metre 20 cm ID plastic column filled up with coal has been carried out. As the coal ages (becomes oxidised) its reactivity towards oxygen decreases and changes in the oxygen concentration profile are noticed.

Experiments have been carried out up to 8 months and from the results obtained, a simple pseudo-steady-state model has been developed to describe the diffusion of oxygen into a reacting coal bed. The findings could prove useful in trying to find a solution to coal and waste dump fire

control.

The second experiment is a simple isothermal oxygen absorption experiment in which the rate of absorption of oxygen on a given coal sample is measured at different initial concentrations of oxygen. The initial concentration of oxygen is varied over a fairly wide range in order to determine the dependence of the rate of oxidation on the oxygen concentration. The rate- limiting step in low temperature oxidation of coal is found to be the absorption of oxygen.

Moisture also plays a role in coal oxidation. Drying experiments were also carried out so as to quantify and investigate the rate of loss of moisture. Models have been developed which try to explain the mechanisms involved in the drying process. The modelling suggest that the bound water model is more appropriate to the type of behaviour exhibited during the drying process.

ACKNOWLEDGEMENTS

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LIST OF SYMBOLS

a	Constant specific to the coal
AN_2	Measured area of the oxygen peak
AO_2	Measured area of the oxygen peak
C	Concentration of oxygen (mol)
C_i	Initial concentration (mol)
C_o	Initial oxygen concentration (mol)
D	Diffusivity coefficient ($m^{-1}.min^{-1}$)
f	Response factor
g	Mass of moisture (g)
g^o	Moisture content of coal (g)
k	Rate constant
k_1	Constant
k_2	Constant
k_s	Reaction rate constant
L	Height of bed (m)
m_i	Mass of coal (g)
n	Order of reaction
p	Equilibrium vapour pressure (kPa)
p_c	Number of reactive sites per unit volume
R	Oxygen consumption rate at time t ($mol.min^{-1}$)
R_o	Oxygen consumption rate at time 0 ($mol.min^{-1}$)
R_i	Oxygen consumption rate at infinity ($mol.min^{-1}$)
S	External surface area of coal (m^2)
x	Position along the column (m)
X	Amount of oxygen absorbed (mol)
X^F	Thickness of coal specimen (m)

CHAPTER I

LITERATURE SURVEY

1.1 Introduction

The oxidation of carbonaceous matter in coal is primarily responsible for the initiation of spontaneous combustion. There are also other factors which are believed to assist in the generation of heat, these are bacterial action on coal, sorption of water vapour, crushing of coal due to earth movements and oxidation of pyrites present in coal. The importance of the role played by low temperature oxidation of coal in spontaneous combustion cannot be underestimated. Heat production and its control remains a problem in the coal mining and consumption industry. In some cases the spontaneous heating of coal has deteriorated into spontaneous combustion or seriously affected the quality of coal. Loss of machinery, life, equipment and negative environmental impact in general has also been witnessed in several incidents.

As a way of trying to monitor coal dumps and predict the likelihood of combustion to occur, a large amount of effort has been devoted to this area of study by scientists and engineers. This has lead to proposing controlling mechanisms which have turned out to be very satisfactory for some coals while being applicable in broad terms to all coals.

Many theories have been put forward in trying to explain

spontaneous combustion in coal. Until the middle of the last century, the popular belief was that the presence of iron pyrites in the coal was responsible for spontaneous heating in coal, Schmidt (1945). It was thought that heat generated during pyrite oxidation was sufficient to raise the temperature of the coal to a level where it will undergo spontaneous combustion. Further studies showed that heat generated during pyrite oxidation was not on its own sufficient to cause an outbreak of fire in coal.

A new explanation had to be found to explain the phenomenon. Currently it is believed that the mechanism responsible for heat generation is the combining of coal with atmospheric oxygen. This is believed to be the principal process responsible for the self heating of coal. There is theoretical and experimental evidence to support the general assumptions being made in identifying the pathways and understanding the overall processes involved. Mathematical models of varying complexity have been proposed based on the above mentioned line of thinking, (Nordon 1979, Edwards 1983, Edwards 1990, Schmal 1989, Akgun and Arisoy 1991, Brooks and Glasser 1986, Brooks et al 1988).

1.2 Factors Affecting the Oxidation of Coal

The reactivity of coal is due to its functional groups. The groups are formed by combinations of atoms and have different chemical characteristics depending on the nature of bonding within the structures. This research is based mainly on the reacti.. f these functional groups with atmospheric oxygen and commercial air containing various concentration of oxygen at constant temperature (isothermal conditions). Analytical techniques are applied to monitor the progress of the reaction and identify the gaseous reaction products where possible.

1.2.1 Partial Pressure of Oxygen

Observations in isothermal oxidation experiments carried out at varying concentrations of oxygen have been done previously. Carpenter et al (1964) concluded that consumption rate of oxygen increases with the square root of oxygen concentration and suggested that this is due to dissociation of oxygen molecules into atoms prior to chemisorption. The rate of oxygen consumption in isothermal experiments was found to increase with a corresponding increase in oxygen concentration.

1.2.2 Bacterial Action

Heating due to bacterial action on carbonaceous material is a common phenomenon. This is witnessed by the heating process occurring in wood and haystacks. In coal, bacterial action is known to have a heating effect though less pronounced than in other carbonaceous material. Potter (1980), inoculated coal with a pure culture of diplococcus, a bacteria, and observed that there was a heating effect from the bacterial activity.

1.2.3 The Pyrite Oxidation Theory

Coal has been known to contain iron pyrites in the order of up to or more than 12%, Francis, Wilfrid (1961). This is not the main source of heating in coal as was the general belief in the past but the heat generated by the pyrite oxidation process cannot be totally ignored. Its contribution to the overall heat produced can be significant. When pyrite is present in coal in a finely divided state there is rapid absorption of oxygen and the reaction yields 16.7472 joules/ml of oxygen consumed. Products more bulky than the reactants are produced. The bulky products result in breaking open the coal in which they are embedded thereby exposing fresh reactive sites, Coward, (1957). The reaction in moist air can be represented as follows:

$$2FeS_2 + 7O_2 + 16H_2O \rightarrow 2H_2SO_4 + 2FeSO_4.7H_2O + 1.323\ kJ$$

The immediate acidic medium around the coal due to the sulphuric acid produced from the above reaction is likely to act on the functional groups of coal to produce derivatives such as esters.

1.2.4 Product Gases

This area was not directly investigated during the various oxidation tests carried out in this work but the findings by previous researchers seem relevant to this work. Carbonic gases have an inhibiting effect on oxygen absorption. Itay (1983), observed that replacing the oxygen in a run with fresh oxygen revived the reaction which had gone to a minimum rate. He concluded that some products of the reaction were inhibiting the reaction. To confirm this, 5% by volume of various carbonic gases were added to experimental runs. The results showed that runs in which carbon monoxide was injected had the lowest rate of oxidation. The runs into which carbon dioxide was added were also affected but not as seriously as those with the monoxide. The rate of production of these gases seemed not to be affected by their presence. This suggested that it was not the oxidation which was affected but the physical absorption of oxygen onto the coal, which is thought to be the initial stage prior to

oxidation taking place.

1.2.5 Particle Size

The surface area of coal in contact with oxygen is a key factor in coal oxidation. Generally speaking the smaller the particle the higher the surface area. As a result susceptibility to oxidation in coal increases with a decrease in particle size. Based on the findings of several researchers, the increase is not as high as expected. This can be supported by the work done by Winmill (1915). After reducing coal size such that there was a 400- fold increase in its external surface area there was correspondingly increase of 1.4- fold in the oxidation rate. In some cases surface area has been related to the amount of oxygen absorbed, leading to derivation of varying mathematical expressions. Yamasaki (1953), came up with the following mathematical explanation for the oxygen absorbed:

$X = aS^{0.404}$

where X is the amount of oxygen adsorbed, S is the external surface area and a is a constant specific to the coal.

1.2.6 The Effect of Moisture on Coal Oxidation

Though its effect is poorly understood, moisture is

believed to play a vital role in the oxidation and spontaneous combustion of coal. Several studies have been carried out to try to understand the chemical changes associated with the effect of moisture on coal oxidation. The general findings, Hyde and Huberts (1993), is that the higher the moisture content of coal the higher the rate of oxidation. High oxidation rates have been associated with heat generation which can cause temperature build up especially in cases of poor ventilation. Nordon et al (1979) pointed out that absorbed moisture exerts a catalytic effect on coal oxidation rate and that there is a transient heat effect that occurs when moisture is absorbed or desorbed from coal.

Arisoy and Akgun (1994), in their model of spontaneous combustion made the assumption that if the coal has enough moisture (0.5 - 8 wt %), exothermic reactions will occur due to the catalytic effect of moisture in the formation of peroxy complexes. The release of moisture from coal results in an increase in the available oxidation surface owing to the opening up of active sites. They believe the major effect of moisture seem to arise from evaporation and condensation.

Different ranks of coal contain varying quantities of moisture, present as either mechanically or as physically

bound water, Gauger (1947). Tne chemically admixed water on the surface and inside cracks and large capillaries has a normal vapour pressure which Gauger termed "free water" with the same physical properties as ordinary water. The physically held water in the internal pore structure of the coal has a vapour pressure lower than normal which he termed "bound water". As a way of trying to quantify the amount of moisture in coal several methods have been used and varying results obtained depending on the conditions of operation and sample physical structure.

The computer simulations by Murtagh (1966) and Schmal et al (1985) to assess effect of moisture transfer in a bed showed that at low temperature, moisture transfer is the dominant heat transfer mechanism in a coal bed. This is attributed to the large latent heat of phase change which is transferred as water evaporates from hotter regions and condenses in cooler zones. This process tends to reverse the heating effect and tends to even out the temperature within the bed which can be explained by the cooling effect of evaporation and heating effect of condensation.

Panaseiko (1974) characterised the various states of water in coal as "chemically bound, sorption water or free". The chemically bound water is linked to the coal

predominantly through hydrogen bonding to oxygen containing groups on the coal surfaces. The amount of water physically adsorbed on the coal surface is determined by the " orientation, dispersion and induction forces of intermolecular interaction (van der Waals forces)". Besides the drying conditions, the amount of water released also depends on the state of forces holding the water on to the coal surface.

The theory of hydrogen bonding have been put forward by several researchers, Rukin (1974) and Parkash (1974). Both workers postulated that water molecules bond to -OH and -COOH sites on the coal, the adsorbed water molecules become secondary adsorption centres for additional hydrogen bonding with successive water molecules. Artificial blocking of the oxygenated groups with chemical agents resulted in less bound water according to the findings of Rukin (1974).

1.2.7 Other Factors

When a carbonaceous dump is considered several factors mainly related to the prevailing atmospheric conditions come into play. Wind pressure on inclined surfaces of dumps lead to air penetration into the dump, hence supplying the dump with oxygen. Other processes which can alter the dump air composition include molecular

diffusion as a result of a concentration gradient. Thermal and barometric breathing are other ways in which ventilation occurs.

1.3 Methods of Water Removal From Coal

The relation of moisture content to the reaction kinetics involved in the oxidation of coal has already been discussed. To get fairly accurate results for the reaction kinetics particular attention has to be paid to the drying conditions as these can affect the results obtained. Accurate measurement of coal's moisture content is also important for the determination of calorific values of coal upon which the selling price is determined.

Two main methods have been used, namely thermal treatment of coal and evacuation based processes. These methods can be used simultaneously or separately. Results obtained from thermal based drying processes are likely to be less accurate as high temperatures are used and this has an effect on oxidation or on the volatile content of the coal. An inert environment, usually achieved by continuously purging the coal with high purity nitrogen helps in obtaining more accurate results.

Several mechanisms have been proposed to explain the

stages involved in the drying process. The assumption made by Cheong et al (1986), that the process of evaporation starts from the external surface and recedes gradually to the centre of the particle resulting in the resistance to mass transfer increasing with dryness seems to be applicable in several cases. This is likely to be more applicable to coals which have a more open texture which hold moisture leading to high average inherent moisture.

A number of methods have been used to determine the amount of moisture in coal. The British Standard (1957), recommends the use of air drying for high rank coals. This is only if the coal is coarsely crushed. For low rank coals, oxygen- free nitrogen must be substituted or alternatively the coal is dried in a vacuum oven.

Besides the thermal and evacuation-based methods, Gray and Whelan (1955), found out that a maximum rise in temperature was recorded when coal was mixed with concentrated sulphuric acid. The rise in temperature was linearly related to the moisture content of the coal. The method was found to be applicable to coal of moisture content varying from 15-20%, the level of accuracy was found to be around 5%.

1.4.0 Mechanism of Low Temperature Oxidation

Coal is a complex heterogenous substance whose structure is not yet fully understood, this in turn has hindered a comprehensive understanding of its reaction with oxygen. However, much work has been done on coal oxidation, hence a substantial amount of literature is available based on the findings of several researchers. Coal is a heterogenous stratified organic rock with large internal surface area in the case of low rank coals. The major component of coal is carbon which varies from 70% in lignite to 96% in anthracite. For bituminous and sub-bituminous coal the carbon content is also between the ranges given above. Oxygen-coal reactions at moderate temperatures are believed to be generally of two types, one involves the formation of oxy-functional groups on the surface of the coal, while the other one is a reaction which produces gases such as CO_2, CO and H_2O Carpenter, et al (1964). The total consumption of oxygen is then given by the sum of the oxygen consumed by these two reactions.

There is universal agreement that oxygen is adsorbed onto the solid surfaces during the oxidation of carbons and coals. The adsorption is an exothermic process which is always rapid in the initial stage. This adsorption process is due to the presence of residual field forces

at the surface of the coal. Physical adsorption is the dominant process at low temperature. Physical adsorption which is believed to occur in a single or multiple layers is due to van der Waals forces, Karsner, (1980). The process is reversible and the oxygen can be recovered by physical means such as evacuation. The chemisorption process forms ionic and covalent bonds with the coal on the carbon surface and the oxygen is held firmly to form a one molecule thick layer. The oxygen is only recoverable at reduced pressure in the form of CO_2 and CO when heated to 950°C, Walker, et al (1969). This finding was consistent with the finding by Sevenster (1961), that the amount of oxygen recovered by physical means varied inversely with temperature, but above 50°C adsorption was irreversible.

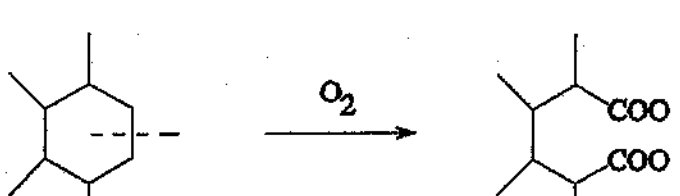
The experimental work carried out is not completely new but there are close similarities for instance with the column experiment by Kok, et al (1989). In their case they drilled a vertical hole in a coal pile and put measuring probes into the hole which was then resealed. Gas was drawn from the coal pile via probes to be analysed. The initial measurements showed that O_2 , CO_2 and $C_x H_y$, mainly methane occurred in all piles. In their experiment O_2 and CO_2 were found to increase with time this is consistent with the findings by the author of this dissertation though the increase in CO_2 was found to

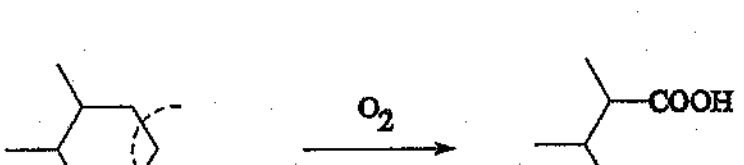
be not that significant in this work.

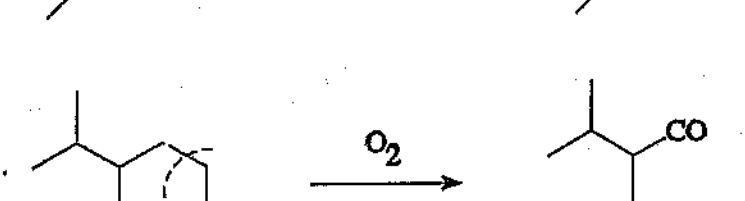
1.4.1 Oxy-Functional Complexes

Coal in its natural state contains varying amounts of oxy-functional groups which tend to increase as additional oxygen is adsorbed during the oxidation process. The chemisorption process leads to formation of such groups as R-OH (hydroxyl), R-COOH (carboxyl), R-OCH_3 (methoxyl), esters, ethers, peroxides and hydroperoxides. These were reported in the findings by, Adams et al (1955), Blom et al (1957), Mukherjee et al (1957), Bhowmik et al (1959), Mazumdar et al (1959), Marinov (1977) and Kucher (1977).

The IR studies of oxidised coals by Adams et al (1957), revealed that there is a large increase in the aromatic carboxylic acid. From these findings they proposed that aromatic rings are ruptured and groups are formed at the expense of peripheral CH groups on condensed aromatic nuclei. The following three schematic reaction proposals were then put forward as possible mechanisms of carboxylic acid formation:

1. 

2. 

3. 

Van Krevelen (1961), proposed the mechanism given below to be another route followed during the oxidation of aromatic groups:

Bhowmik et al (1959), also cited the above mechanism after measuring the amounts of carboxyl, hydroxyl and carbonyl groups formed at 200°C for oxidation times between 100 and 300 hours. They found aromaticity to be decreasing with time during the 300 hour test. The decrease in aromaticity could only be attributed to rupture of the rings as predicted by Adams et al (1955).

Chamberlain et al (1976), following the discovery of an increase in carbon monoxide, put forward the suggestion that at increased temperature an additional reaction takes place besides those mentioned. They put forward the following summary as the likely mechanism of the reactions involved:

$$R{-}H + O_2 \longrightarrow R^{*} + HO_2^{*}$$

$$R^{*} + O_2 \longrightarrow R{-}O{-}O^{*}$$

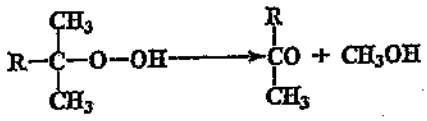
$$R{-}O{-}O^{*} + HO^{*}_2 \longrightarrow ROOH + O_2$$

$$R{-}O{-}O^{*} + RH \longrightarrow ROOH + R^{*}$$

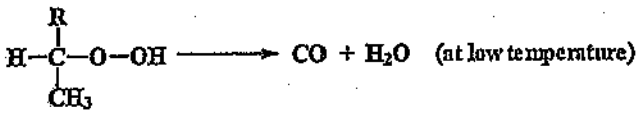
The peroxide ROOH will then decompose in different ways depending on whether it is tertiary, secondary or primary

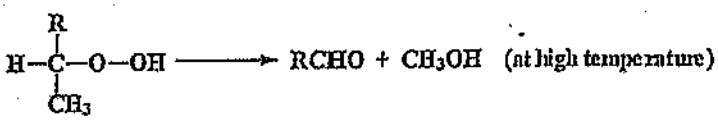
alkyl peroxide. Given below is a summary of the decomposition reactions:

(i) Tertiary alkyl peroxides

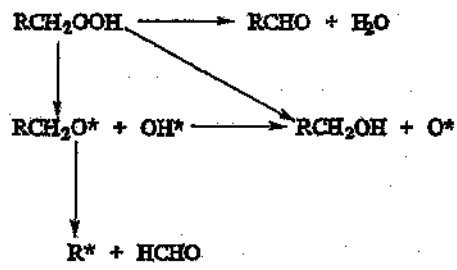


(ii) Secondary alkyl peroxides





(iii) Primary alkyl peroxides



1.5 Literature Survey of Mathematical Models

Several mathematical models for coal dumps have been presented and there is still need to derive other models to suit various conditions of operation and different types of coal. A brief survey of the available models relevant to the work carried out is given below. These models, based on chemistry and chemical engineering principles, are able to describe with increasing accuracy the kinetic behaviour of coal oxidation.

1.5.1 Total Oxygen Consumption Models

A substantial number of models have been proposed for the moderate temperature oxidation of coal. Schmidt et al (1940) correlated their oxygen consumption data with the equation, $X = Ct^b$.

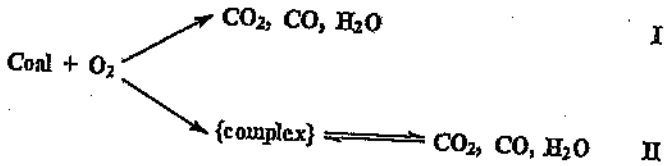
X is the amount of oxygen consumed, t is time, C and b are experimentally determined constants which range from 0.04 to 0.4 and 0.6 to 0.8 respectively.

The model for the rate of oxygen deposition by Georgiadias and Galliard (1953) was given by:

$$\frac{dO_2}{dt} = -k(O_2) + a \qquad [1.1]$$

Where O_2 is the amount of oxygen adsorbed, k and a are experimentally determined constants. The amount of oxygen deposited onto the coal surface is predicted to increase to an asymptotic value of a/k by the above equation.

Kam, et al (1976), put forward the following schematic model where oxidation was taken to be limited to the superficial surfaces and macropores, (the KHP model).



There are two paths which are involved in the model, I , which is a direct burnoff reaction and is a combination of zero and first order reactions with respect to the surface oxygen concentration. The other path, II,

consists of chemisorption and formation of CO_2, CO and H_2O via an oxygenated complex intermediate.

Taylor and Thou's (1952) interpretation of the Elovich equation and chemisorption is the basis for the formation of active sites and their reactions with oxygen in path II. For temperatures less than 230°C, the equation for the total oxygen consumption rate in a fixed bed reactor was given as:

$$R(t) = R_1 + \frac{(R_o - R_1)e^{-kt}}{1 + \frac{(R_o - R_1)}{R_i}(1 - e^{-kt})} \quad [1.2]$$

Where R_o, R and R_1 are oxygen consumption rates at time zero, time, t and infinity respectively and k is a rate constant. The KHP model only fits total oxygen consumption rate parameters R_o, R_1 and k. The model fails to fit the distribution of consumed oxygen into various products. The activation energy is modelled using the Arrhenius equation.

Taylor and Thou (1952) concluded that deviations from the Elovich equation were the result of a change from one type of site to another. Harris, et al (1975) disputed this and attributed the deviations to pore diffusion. They disputed Taylor and Thou's (1952) conclusions on the

rate controlling process as according to the interpretation by Harris et al (1975), the Elovich equation is just an empirical relation. The same sentiments were shared by Clark (1970), he put forward the conclusion that the Elovich equation is just for correlating data and is not valuable in settling questions of mechanisms.

Itay (1984), proposed with a model in which he suggested that in a non catalytic environment, the reaction of particles in a surrounding fluid can be explained in terms of an unreacted core in which reaction starts from the outer skin of the particle. The zone of reaction moves into the solid and is likely to leave behind completely converted material and inert solid. The oxidation rate decreases as we move to the core of the coal particle due to the formation of oxidation rims. The rims act as a barrier for further diffusion of oxygen. Thus the oxidation rate decreases due to a shrinking core. The general reaction can be represented as follows:

$$\text{Coal} + O^*_2 \rightarrow \text{Oxycoal} \rightarrow CO_2,\ CO,\ H_2O$$

O^*_2 is the physically adsorbed oxygen.

The intermediate physical absorption accounts for the overall rate of reaction and the oxy-coal is the major

source of CO and CO_2. The O_2 absorption was predicted to be of the order 0,5 with respect to the O_2 concentration. Finally a simple Arrhenius form was ruled out as a measure of the overall change of rate with temperature due to the ageing effect on the rate of oxidation of the coal. The total oxygen consumption chemical reaction for the shrinking core model as put forward by Itay (1984), can be represented as follows:

$$r = \frac{m_o}{\rho_o} \frac{\frac{k_s C_{(o)}}{1 + xK}}{sD} \qquad [1.3]$$

Where:

s - specific surface area.

m_o -mass of coal

k_s -reaction rate constant

C - concentration of oxygen

p_o -number of reactive sites per unit volume of coal

D - is the diffusion coefficient

X - fraction conversion

It seems like the shrinking core model has been looked at by different workers, Levenspiel (1972), looked extensively at this model. The basis of his argument being that at any time there exists an unreacted core of

material which shrinks in size with time as the reaction proceed.

A good model should generally be as close to reality as possible. Karsner, (1980), proposed what he termed the chemical reaction control model in which he concluded that the oxidation reaction is limited by the solid surface. He suggested that in a heterogenous substance such as coal, several types of sites exist and gaseous oxygen reacts with them in a number of ways. He believed that there exists a wide distribution of energy levels in the sites due to the nature of chemical bonding involved and location of each site within the solid.

Karsner went further to lump the sites into four types categorised as to whether they react with oxygen to:

(a) form CO_2 and CO in direct burn off reaction
(b) physically absorb O_2 onto the coal surface
(c) chemically absorb O_2 onto the surface
(d) form H_2O

These sites are assumed to be randomly dispersed onto the solid surfaces. The oxidation process is believed to consume sites and the process depends on the number of sites remaining.

1.5.2 Drying Models

A number of drying models have been proposed and shown to be applicable in various situations, Arison and Akgun (1993). One of the most common models revolves around the shrinking core behaviour which is believed to be exhibited by the coals both during drying and oxidation reactions.

The drying model proposed by Karsner, (1980), considers what happens during the thermal drying of coal in the temperature range 150 to 300°C. The two main processes occurring are the evaporation of water and degradation of oxygen containing groups on the surface of the coal to form CO_2 and CO. The evolution of these gases occur while drying under an inert atmosphere.

The amount of carbonic gases cannot be accounted for by oxygen trapped in the coal pore structures. The most likely source of this oxygen must be primarily oxy-complexes on the coal surfaces. In this particular model it was found out that the rate of carbonic gas evolution increases linearly with coal oxygen content for all coal studied.

A kinetic model based upon a simple zero and first order decomposition of oxy-functional groups on the coal

surface represents the rates of carbonic gas evolution during drying. The model postulates a first order decomposition reaction below 250°C. This can be represented by the rate equations given below:

$$R = R^{o}\, e^{-k}\, a^{t} \qquad T < 250°C$$

$$R = R + (R^{o} - R)\, e^{-k}\, a^{t} \qquad T > 250°C$$

In this work two models have been looked into which are the bound water model and the shrinking core model. The bound water model is explained in terms of vapour pressure difference between the coal and the air see section 5.5.1 for details. The shrinking core model can be explained in terms of the unreacted core model by Levenspiel (1972). According to this model a reaction proceeds at a narrow front which moves into the solid particle. The unreacted core shrinks with time as the reactant is completely converted as the front pass by. For the model in this dissertation the moisture rich part of the coal can be taken as the unreacted core which shrinks with time as water losses occur during the drying process.

1.6 Objectives of This Project

It is well known and documented that there is a universal

problem of spontaneous combustion among coal practitioners. coal Spontaneous combustion of coal is a problem among coal practitioners.

The basic aim of this work is to understand and model the low temperature oxidation of coal as well as the rate of drying. This project is part of an ongoing study in coal chemistry kinetics so as to obtain information necessary for people who work with coal in order to reduce chances of spontaneous combustion from occurring, eg by controlling oxygen flow into a coal bed or covering the coal pile with a protective layer of reactive material.

CHAPTER II

EXPERIMENTAL PROCEDURES

2.0 Introduction

Three different aspects of spontaneous combustion of coal were investigated in this dissertation.

(a) An experiment was performed to measure oxygen profiles in a column of coal and thereby investigate the relationship between oxygen diffusion and reaction with time.

(b) Experiments were performed to measure the kinetics of coal oxidation. Factors such as oxygen concentration were varied and the effect of this on the reaction rate was determined.

(c) The drying rate of coal was measured in order to investigate the kinetics and mechanisms of the drying process.

These three aspects are very important on understanding and modelling the spontaneous combustion of coal.

2.1 Sampling

Samples were obtained from one mine only, the New Vaal Colliery in the Orange Free State. The mine used to be an underground mine which was later converted into an open

cast mine. The samples were collected from the piling stacks as the coal came from the crushing and washing section of the mine. The samples were assumed to be fresh. The coal can be classified as of very low standard based on the fact that the ash content is very high, 40% on the average and calorific values are in the regions of 16kJ/mole.

Ground coal samples were collected from the piling stacks as the coal came off the conveyor belt. They were put straight into polythene bags, crushed dry ice was immediately sprinkled into the bags to reduce the reaction of the coal with oxygen to a minimum, prior to onset of the experiments. The bags were then tightly sealed. Several samples were collected using the above mentioned procedure. For the drying experiments large coal boulders were obtained just before the coal reached the crushing stage. Samples collected were then immediately transported to the laboratory where the experiments were to be conducted.

2.2 Coal Storage and Preparation

The contact of the coal with the environment was minimised so as to avoid premature oxidation of the coal before the onset of the experiments. The coal samples with the exception of the boulders for the drying

experiments were too moist because of the washing and as a result had to be dried to acceptable levels. This was done in a constant temperature room at a temperature of 10°C. The temperature was kept low to minimise any premature oxidation which was likely to take place. The drying process took about 72 hours, samples for the drying experiment were not subjected to the preliminary drying process. During the drying stage the temperature was kept at 10°C (not lower) to avoid cracking the coal and exposing new reactive sites as this would lead to a deviation from the original state of the material from the dumps. After drying the coal was put back into the bags which were then stored in air tight cupboards kept flushed with oxygen-free nitrogen from a cylinder. The nitrogen was first bubbled into a Drechsel bottle containing water before going into the cupboard so as to maintain the humid conditions prevailing in the mines.

2.3 Oxygen Reaction and Diffusion Experiment

The underlying philosophy of this investigation is that, oxidation of coal is a heat generating process and if moisture content in coal is high the process occurs at an even faster rate. This can lead to spontaneous combustion of coal. Distribution of oxygen and products of oxidation in the coal bed may possibly provide information required to take precautions.

There was no need for further milling the coal which was used for the oxygen concentration gradient experiment. The particle size of the coal was found to be convenient for the nature of the work which was to be carried out. Further crushing could have lead to a disturbance in the original structure of the coal by exposing "fresh" active sites. The samples needed to be as close as possible to the original coal in order to get a true reflection of what was happening to coal in the dumps of that particular type of coal.

2.4 Isothermal Oxidation Experiment

The isothermal experiment carried out is closely related to the one carried out by Smith, (1983). In Smith's experiments oxygen concentration change was monitored on a gravimetrical basis. The apparatus was modified so as to monitor change volumetrically. The results obtained in both cases were similar. The findings were that oxygen concentration fell with time in both cases.

The samples for the isothermal oxidation experiments were ground in a roller mill. This was done after initially trying to perform runs on samples which had been sieved. This most likely lead to a non representative sample being obtained. This was probably due to softer coal portions being the source of the smallest particles. The

ground sample was kept in a glass jar under nitrogen to maintain an inert environment to avoid premature oxidation.

2.5 Drying Experiments

For the drying experiments, the coal boulders were cut into small rectangular blocks of area of 12cm^2 on average and thickness ranging from 2.5 - 4.5 mm. This was done so that one could obtain two dimensional surfaces of coal of known surface area for the experiments. The other four edges with the small areas were coated with silver paint so that moisture lost through these edges was minimised.

2.5 Proximate Analysis

The analysis was carried out by New Vaal Colliery Laboratory which was involved in the acquisition of samples used in the experiments carried out. The coal as it came from the mine was found to have the following parameters:

(a) % Moisture - 8.0

(b) % Ash - 40.0

(c) Calorific value - 16kJ/mole.

CHAPTER III

Oxygen Concentration Profile Experiments

3.0 Introduction

A column was filled up with coal and the top of the column was left open to ambient air as discussed in section 3.2. The oxygen concentration in the column was monitored over a period of several months as a function of time and position. The experimental methods will be discussed in this chapter.

By looking at how the gaseous oxygen concentrations varied with position and time in the column we were able to look at the relationship between diffusion of gaseous oxygen into the coal bed and the oxidation reaction and hence variation of reactivity of the coal.

3.1 Experimental techniques

The most important measurement in this experiment is the measurements of the concentration of oxygen as a function of time and position in the coal bed. Because of the manner in which the coal is prepared and stored (as discussed in section 2.1.), it is assumed that when the column is filled up with coal the reactivity does not vary with position. The presence of product gases and their quantity can be an indicator of extent of oxidation in the coal bed.

3.1.1 Gas Chromatographic analysis of gas samples

Gas samples were obtained from different heights in the reactor and analysed for O_2, CO_2, CO and N_2. For the analysis a custom made Gas Chromatograph (G.C.) was used. A Thermal Conductivity Detector (T.C.D.) coupled with a data acquisition unit was used to generate peak data which was stored on floppy disks.

Separation of all gases could not be achieved by the use of a single column hence two columns attached to a 4-port valve were used. The valve made it possible to connect the columns in series or by-pass the carrier gas from one depending on the option required. The columns used were a molecular sieve 5A (1.5m, 1/8" ID column) which was used to separate O_2, N_2 and CO peaks, a Porapaq Q (1.2m, 1/8" ID column) was used to trap CO_2. The temperature of operation was maintained as low as possible, between 20 - 22^0 C to achieve maximum sensitivity of the instrument. The carrier gas used was hydrogen at a pressure of 500 kPa and a flow rate of 20ml/minute.

A precision 1.0ml pressure lock syringe was used for sampling from the reactor. A sample of size 0.5ml was injected into the G.C.

3.1.2 Calibration of the Gas Chromatograph

Ambient air was used for the calibration of the G.C., and it was assumed that it contained 21% oxygen. The G.C. was calibrated by calculating a response factor for oxygen. The response factor was calculated using the assumption that the response of the detector was linear. This was checked by using different sample sizes and seeing that the ratio of the areas of the oxygen and nitrogen peaks remained the same.

$$[O_2] \propto AO_2 \qquad [3.1]$$

$$[N_2] \propto AN_2 \qquad [3.2]$$

$$[O_2] = k_1 AO_2 \qquad [3.3]$$

$$[N_2] = k_2 AN_2 \qquad [3.4]$$

$$[O_2] = \frac{k_1 AO_2}{k_1 AO_2 + k_2 AN_2} \qquad [3.5]$$

$$[O_2] = \frac{AO_2}{AO_2 + \frac{k_2}{k_1} AN_2} \qquad [3.6]$$

$$\frac{k_2}{k_1} = f \qquad [3.7]$$

Where: AO_2 is the measured area of the oxygen peak.

AN_2 is the measured area of the nitrogen peak.

k_1 and k_2 are constants.

f is the response factor.

Assuming the air samples to be 21% oxygen and 79% nitrogen an average response factor (f)= 0.8555 was obtained and was used in the final calculations and for calibration purposes. (see appendix A1). This was done regularly throughout the experimental work. The error of the Gas Chromatograph was found to be +/-5% basing on the calculation of the response factor, see also appendix D.

3.2 Oxygen Reaction and Diffusion Experiment Apparatus

The apparatus comprised two different units, the reactor shown in Fig. 3.1 and a Gas Chromatograph unit interfaced to a computer. The reactor was constructed of heavy duty plastic and sampling points were drilled into the wall at 100mm interval. The sampling points had septa so that there was no exchange of air with the environment. The column was of 250mm diameter and 3000mm in height. The G.C. was assembled in the chemistry department and a computer which could run the Hyperplot package was interfaced to it. The G.C. as mentioned before had two columns (Porapaq Q and Molecular sieve) linked by a four port valve which made it possible to separate CO_2 from O_2, N_2 and CO by controlling the path of the carrier gas.

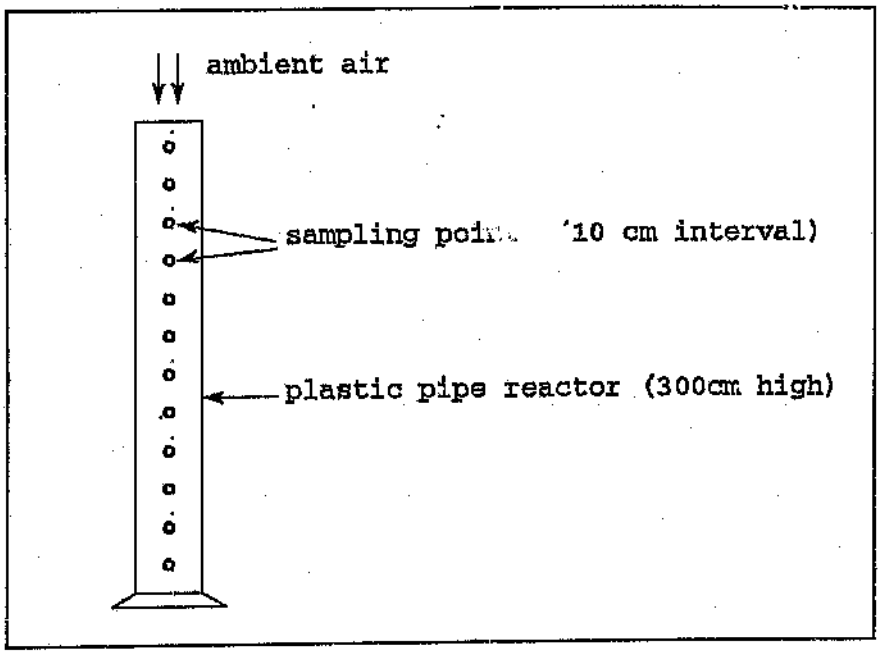


Fig. 3.1 Reactor for gaseous concentration measurements

3.3 Experimental Procedure

The coal samples were taken out of the storage cupboard where they were stored under nitrogen and quickly charged into the reactor which was positioned close to the G.C. A precision 1.0ml pressure lock syringe was used for sampling from the reactor. Samples of 0.5ml were successively withdrawn in descending order from the highest point of the reactor. Just after starting the experiment no CO_2 was expected since the reaction was

still in the early stages of oxygen adsorption. There was thus no need for selective elution of the gases in the first week. The gas samples were allowed to pass through the Porapaq Q and Molecular Sieve for the first 7 days. Thereafter the valve was used for all samples as the chances of getting CO_2 as one of the reaction products was increased. The valve was turned 2.5 minutes after injection, to by-pass the carrier gas around the molecular sieve and then after 5.5 minutes to join the columns in series.

3.4 Results

The concentration profile was initially monitored on a daily basis then the frequency was reduced until a point where it was monitored twice per month as discussed in chapter two. From the results obtained, the concentration of oxygen was calculated at varying heights. The final monthly results obtained were averaged, this was mainly because there was a fair degree of scatter in the results and the profiles only changed very slowly. The averaged results (appendix A2 and A3) were then plotted as a function of height. The graphical results for the two separate runs carried out are shown in Figs. 3.2 and 3.3. From these results it can be seen that, as the coal ages, oxygen penetration into the coal increases with time but the figures over 21% could be due to experimental error.

As a result there is a change in the oxygen profile of the bed and there is a general tendency for the oxygen concentration to increase at the various points. The variability in the properties of the coal itself is also likely to lead to a variation in the reactivity of the coal at varying heights of the bed. This will influence the oxygen profile. The best explanation for the overall behaviour is that the reactivity of the coal falls off with time, as is well known,(see for instance Itay (1983)), that is the coal is ageing. There was no carbon monoxide detected during the course of the experiment. Traces of carbon dioxide were detected up to a height of 100cm from the fourth month but its occurrence did not follow a consistent pattern and there was no specific trend in its occurrence.

For the first three months there does not seem to be much change in the reactivity of the coal as can be seen by the change in concentration with height which does not vary much with time. The variation in the oxygen profile as from the fourth month seems to increase. This can be seen to be the case in both Figs. 3.2 and 3.3. The rate of oxygen diffusion varies in magnitude between the two coals but the qualitative findings are similar. Despite the fact that the coal was collected from the same mine the oxygen diffusion rate is about 30% higher in the first run.

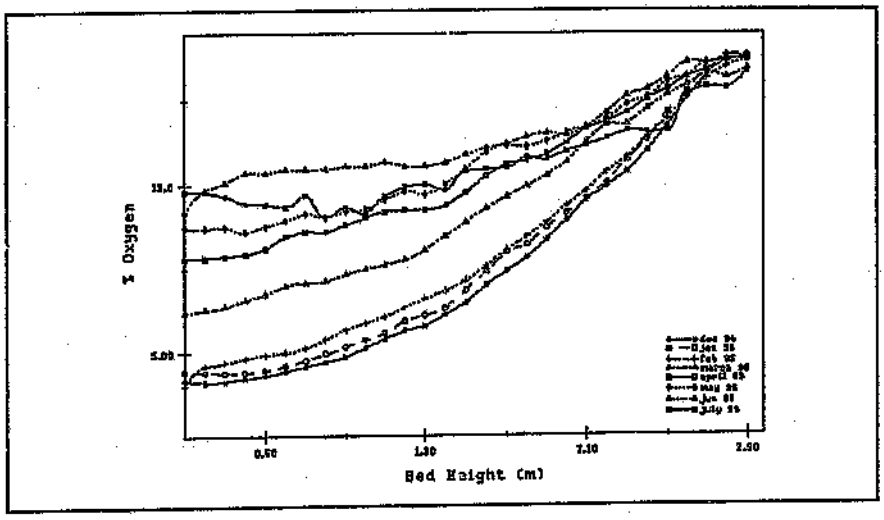


Fig. 3.2 Oxygen concentration profile for run 1

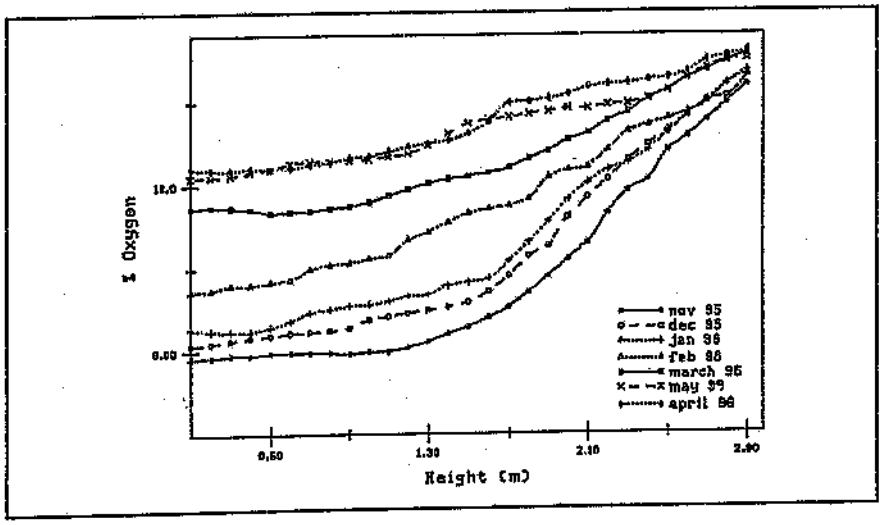


Fig. 3.3 Oxygen concentration profile for run 2

3.4.1 Mathematical Modelling

There has been a lot of work in the literature in trying to find an expression for the kinetics of gaseous oxygen with coal the work done by Javin (1980), Brooks (1985) can be cited as examples. It seems that the concentration dependence is somewhere between half and first order. Furthermore as the coal reacts with oxygen its rate decreases and this is referred to as the ageing affect. Finally this rate is also quite sensitive to moisture content of the coal. Thus it can be seen that it is quite difficult to come up with an explicit rate expression that describes all this behaviour.

For the present we do not need an explicit expression for the reaction rate of the coal with the oxygen, but we do need to take into account that it rapidly deactivates. Because the reactivity declines with the degree of oxidation, the coal particles that react faster will deactivate more quickly. Thus there is a tendency for particles which, for whatever reason, start off having different rates to tend towards similar reaction rates. This result will prove useful in trying to model the experimental results.

Let us now look at the diffusion apparatus. When we start

the experiment, all the coal has the same intrinsic reactivity properties. However because of the diffusion resistance in the bed the oxygen towards the bottom tends to get depleted as seen in the curves in Figs. 3.2 and 3.3 for December 1994 and November 1995 respectively. Thus the reaction rate here will become lower than at the surface because of the dependence of the rate on the oxygen concentration. However, for the reasons discussed above, the rate of reaction at the surface will decay more rapidly than that deeper in the bed, tending to equalise the reaction rates. The overall effect of this behaviour is that it might be a reasonable assumption, to assume that eventually the rate of reaction at every depth is approximately the same, that is we can use a single rate as a function of depth at every time interval.

The overall consequence of this assumption is that at a given point in time we can assume that the rate behaves as if it was zero order with respect to oxygen concentration. If we make this assumption we are in a position to integrate the differential equation describing the behaviour in the column and can test, using the experimental results, how good this assumption is.

If this assumption appears to work well we are then in a

position to plot this average rate as a function of time and see what the ageing effect is. We need to be a bit careful in doing this because as the coal is ageing it will also be drying out as well and this may also affect the rate of reaction. Finally the apparatus is in an open laboratory and so the average ambient temperature will tend to vary with the seasons again affecting the rates. The following assumptions were made in the mathematical model in this study:

(a) The material reacts with a zero order reaction with respect to oxygen and a single average reaction rate over the whole bed was used at each point in time.

(b) The material reactivity decays with time.

(c) The reaction is done under isothermal conditions, (the bed of oxygen absorbing material is kept at room temperature).

(d) We assume the coal reactivity changes very slowly relative to the speed with which the concentration profile sets itself up, (pseudo-steady-state assumption.)

(e) We assume Fick's Law of Diffusion.

3.4.2 Model Equations

Thus making the pseudo-steady state assumption, that is the accumulation terms are negligible at a particular

time t, we can write a mass balance. The rate of change of oxygen concentration with respect to height is given by:

$$D\frac{d^2C}{dx^2} = r \qquad [3.8]$$

Integrating the above equation for constant r gives a general solution:

$$C = \frac{r}{2D}x^2 + ax + b \qquad [3.9]$$

Where: C is the concentration of oxygen.
a and b are constants of integration
x is height from the closed end of the bed
r is the average rate of oxidation at time t.
D is diffusivity coefficient.

Boundary and Initial Conditions:

To solve for the constants, the following boundary conditions have been used.

at x = 0

$$\frac{dc}{dx} = 0 \qquad [3.10]$$

that is there is no diffusion of oxygen across the sealed bottom of the bed.

$$but \quad \frac{dC}{dx} = \frac{r}{D}x + a \qquad [3.11]$$

$$\therefore \quad a = 0$$

$$C = \frac{r}{2D}x^2 + b \qquad [3.12]$$

The other boundary conditions that could be used is:

at $x = L$ $\qquad C = 0.21$

The ambient oxygen concentration is always assumed to be 21%.

$$\therefore \quad 0.21 = \frac{r}{2D}L^2 + b \qquad [3.13]$$

$$or \quad b = 0.21 - \frac{r}{2D}L^2 \qquad [3.14]$$

$$\therefore C \quad at \quad x = 0 \quad is \; b$$

The model can be most easily tested by plotting the measured concentration, C Vs the square of the height x^2. A straight line suggests that the assumptions leading to

the model might be reasonable. This can be seen to be a reasonable approximation from the graphs in Fig. 3.4 and Fig. 3.5.

Now that we see that the results fit the model reasonably well it is of interest to obtain values of this average rate as a function of time and plot them. We can do this directly from Figs. 3.4 and 3.5 as the slope of the straight lines are equal to r/2D as we would not expect the diffusion coefficient, D to vary with time for the two different runs, we can plot the slope versus time. We are then effectively seeing how r, that is the average rate varies with time.

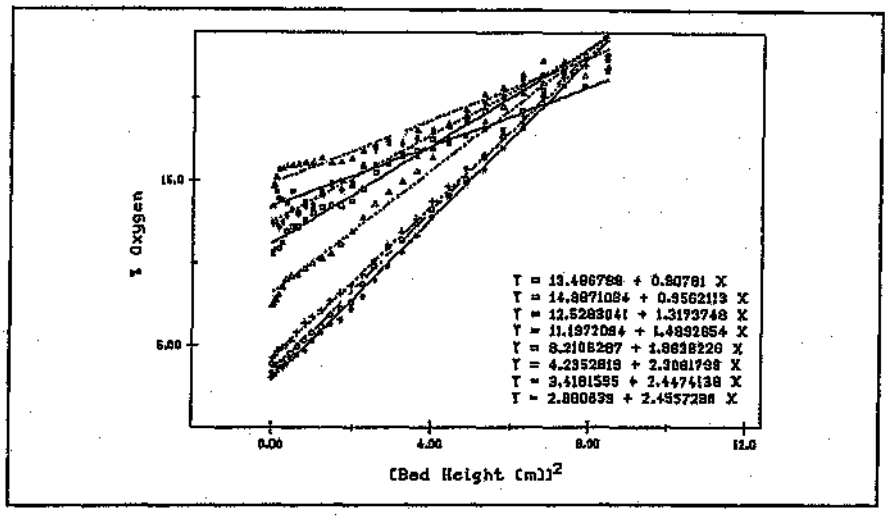


Fig. 3.4 Testing the model for data obtained from run 1

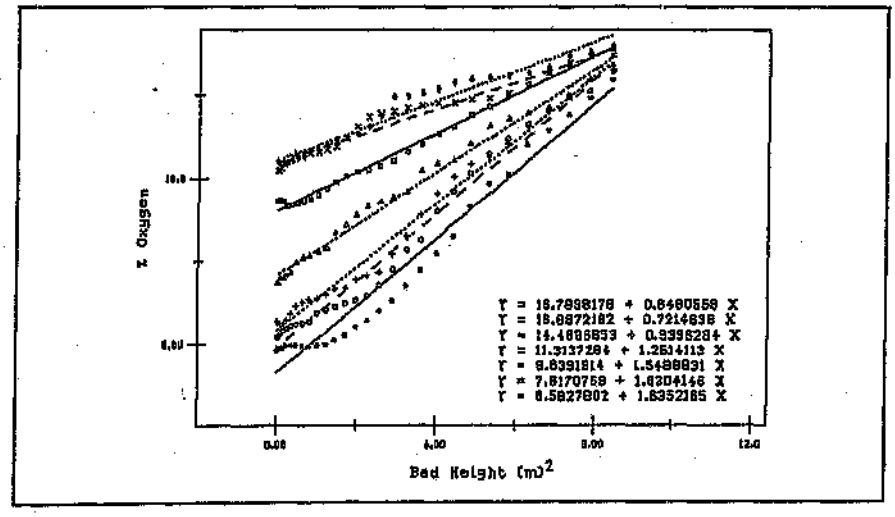


Fig. 3.5 Testing the model for data obtained from run 2

Table 1: Values of *b* and *r/2D* for run 1

MONTH	b	r/2D
1	2.88	2.46
2	3.41	2.45
3	4.23	2.31
4	8.21	1.86
5	11.19	1.49
6	12.52	1.32
7	14.88	0.96
8	13.48	0.91

Table 2: Values of *b* and *r/2D* for run 2

MONTH	b	r/2D
1	6.79	1.66
2	7.82	1.63
3	8.64	1.55

Table 2 continued overleaf...

Table 2 (continued)

MONTH	b	r/2D
4	11.31	1.25
5	14.47	0.94
6	16.88	0.72
7	16.79	0.65

The plot of the gradients versus time for both runs show the same type of S-shaped curve though the material in run 2 is about 30% less reactive, (fig.3.6).

Now recall that r is the average reaction rate in the bed. The value r in equation 3.12 should also be that at the surface of the bed where the coal is exposed to the oxygen concentration in pure air. Even though this is a result taken in pure air it is somewhat different from the situation that is found in other experiments where both the oxygen and moisture concentration have been kept constant Itay (1983), Smith (1993). In particular the other workers have found a steady decline in rate not this S-shape. Now it is known, Itay (1983), that the moisture content has a large effect on the reaction rate. We also know that the initial coal was very moist as it

came from the coal washing plant, so we can speculate that during the first few months the coal bed was drying out. Now it has been shown in fig.3.6 that the reaction rate for constant oxygen concentration is actually depressed for large moisture contents, goes through a maximum at intermediate values and then falls off as the coal dries even further. We can thus speculate that during the first flat phase in fig.3.6 the moisture loss and ageing effects are acting in opposite directions giving a fairly flat section. This is followed by a period in which the rate drops rapidly as during this period the effect of moisture loss and ageing are in the same direction. In the flatter final section the coal moisture has perhaps reached an equilibrium with the air and we are only seeing an ageing effect. Clearly to verify this explanation more work will need to be done.

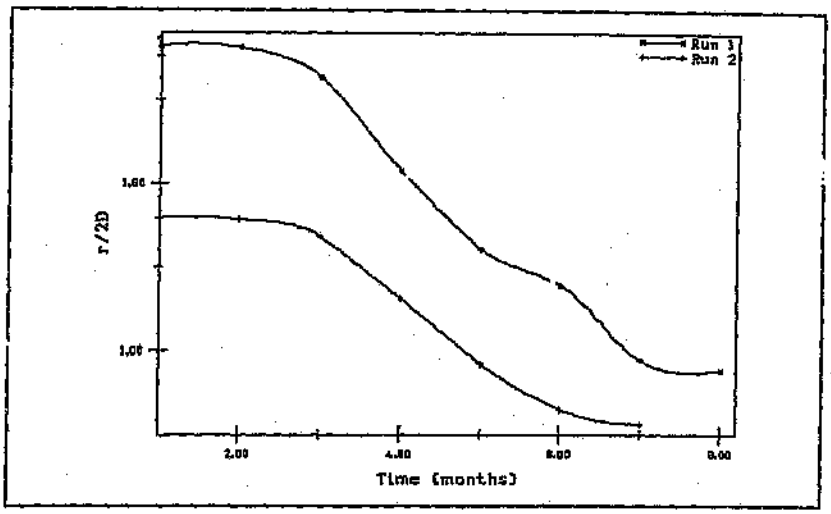


Fig. 3.6 Variation of absorption rate (run 1 & 2) versus time

3.4.3 Fitting the mathematical model to the results

For further verification to check whether the mathematical model is satisfactory, the experimental results obtained were fitted to the model. There are two parameters (r/2D and b) which had to be estimated and this was done using a linear least square regression giving the results shown in Figs. 3.4 and 3.5. The graphs were generated from the experimental data. The values for the different months for b and r/2D are given in Tables 1 and 2.

The best fit of the model for the different months is shown in Figs. 3.7-3.12 and the rest of the fits are given in Appendix A4. The first three months results for the first run fit the model very well and the values obtained for b are very close to those of the model. The results for run 2 also fit the model but are not as good as those in run 1. As the coal ages there is a tendency for the results to drift from the model which is especially evident at the top of the reactor.

RUN 1

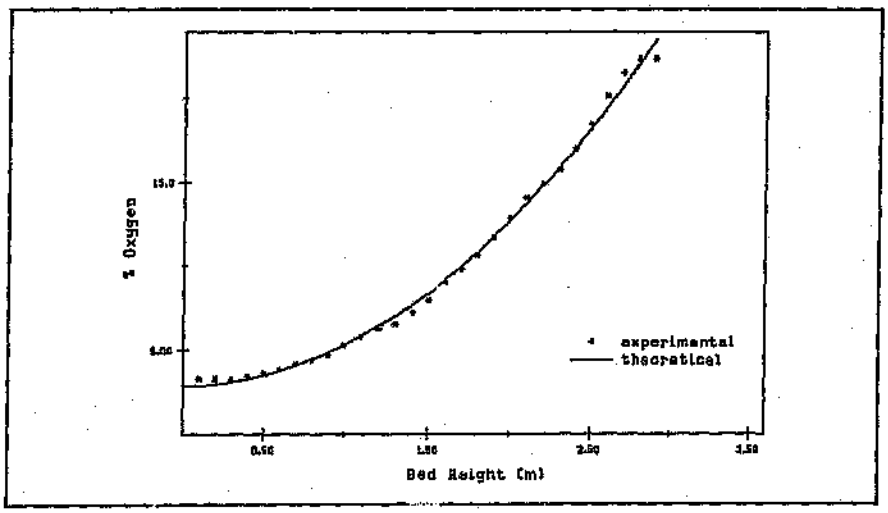


Fig. 3.7 Fitting for oxygen profile for December 1994

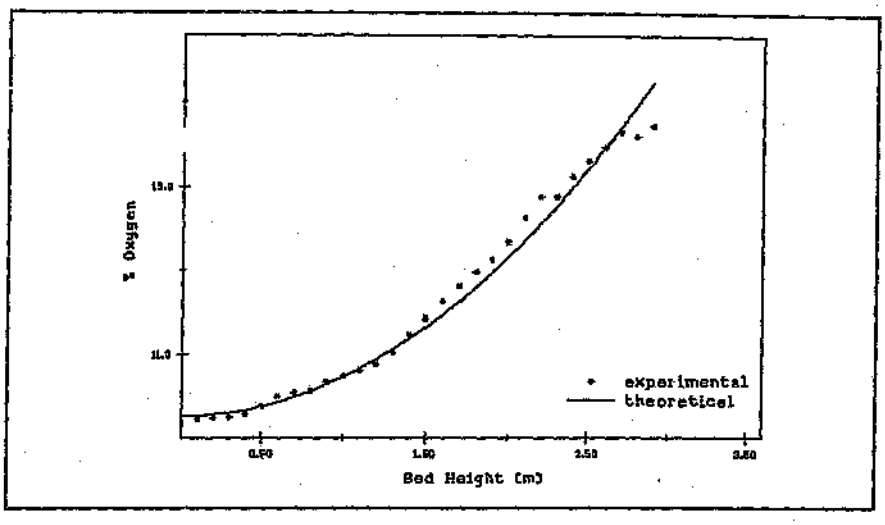


Fig. 3.8 Fitting for oxygen profile for March 1995

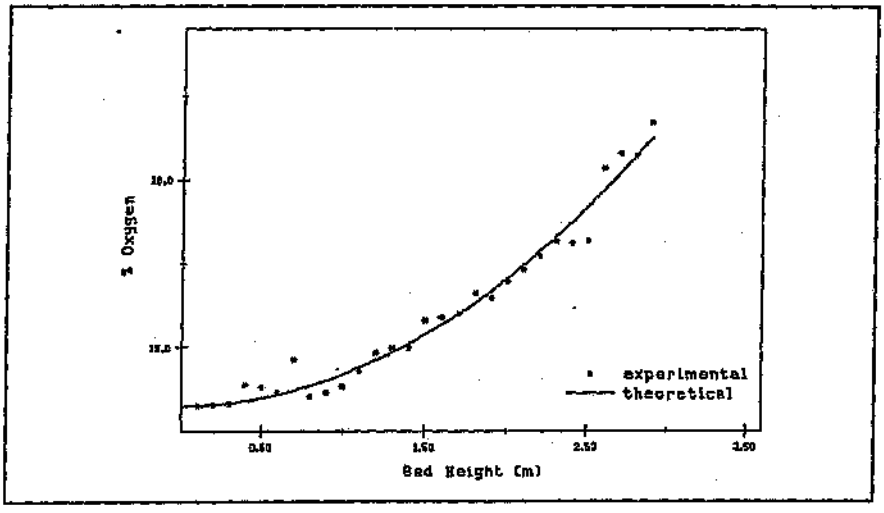


Fig. 3.9 Fitting for oxygen profile for July 1995

RUN 2

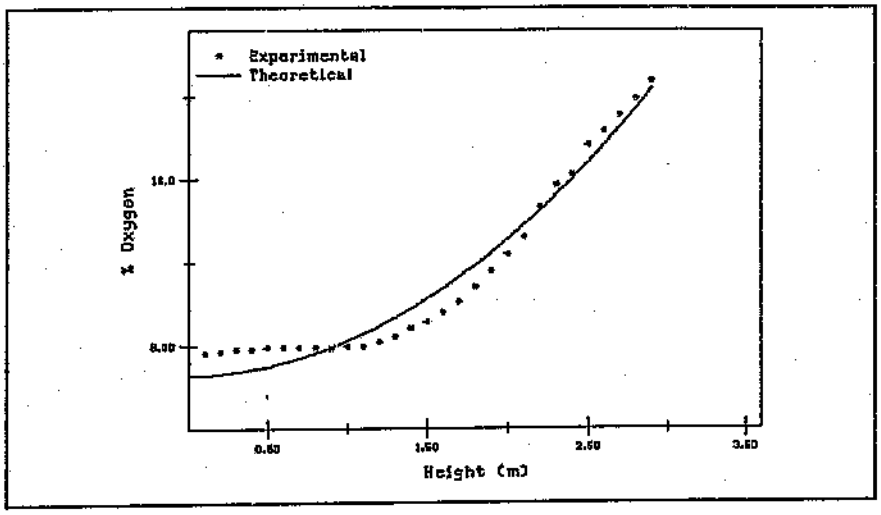


Fig. 3.10 Fitting for oxygen profile for November 1995

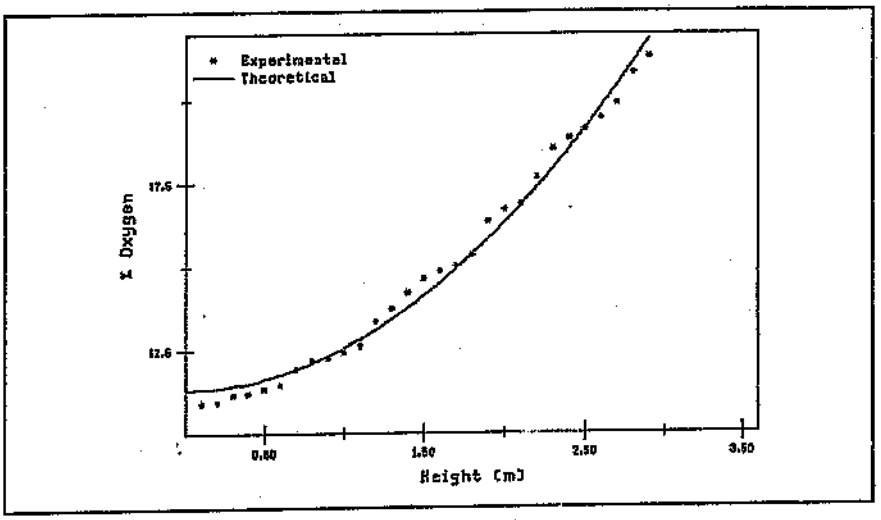


Fig. 3.11 Fitting for oxygen profile for February 1996

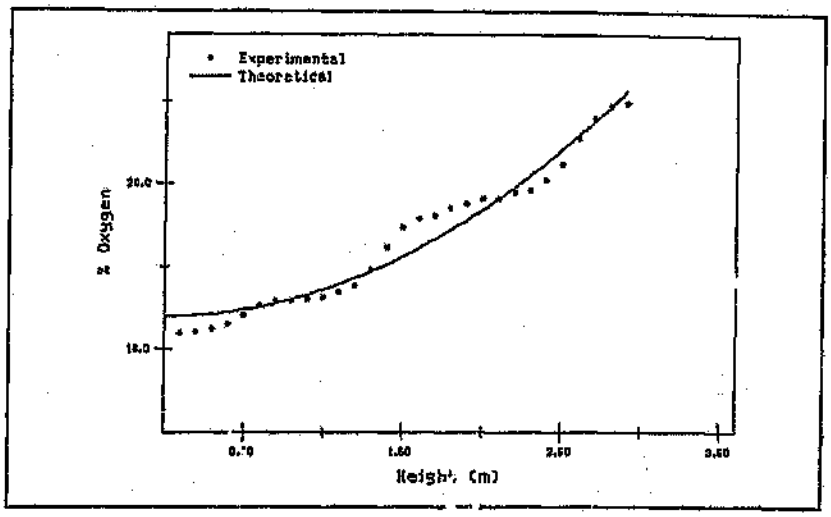


Fig. 3.12 Fitting for oxygen profile for May

3.5 Conclusion

A simple pseudo - steady - state model has been developed to describe the diffusion of oxygen into a bed of reacting coal. The experimental data correlate reasonably well with the model and the results yielded curves which fit the model quite well. This suggests that the assumptions made prior to modelling are reasonable.

This apparatus constitutes a simple experimental technique for measuring the reactivity of coal or waste material and how it changes with time. The apparatus (or

a larger equivalent) can easily handle run-of-mine material directly. The information obtained in this experiment can be used to predict how long it will take for the oxygen concentration to reach a given concentration at some depth in a bed. Parameters to put into models of large scale dumps can be estimated on the basis of this work. This information might prove to be useful in, assessing the safety of coal dumps especially when used in conjunction with other models of related work.

This experimental apparatus could be used to ascertain the effectiveness of adding a reactive layer over the dump. A more reactive and more compact layer than used in this experiment could initially limit the oxygen penetration even more than in these results. However, as the coal ages, penetration of oxygen will increase with time so that a reactive layer covering a bed can never be a long term solution for preventing spontaneous combustion.

The fact that the experiment was carried out under conditions which are close to that which a typical dump is exposed makes it an important diagnostic tool in evaluating what really happens in coal dump. In fact the technique could be seen as a very simple general technique for evaluating the reactivity of real coal

samples. Because there is a strong interaction between many factors, such as moisture content and ageing, it is probably less useful as a technique for fundamental studies. However with some modifications to the experimental procedure such as keeping humidity of the air constant it might have a place in more fundamental studies.

A practical implication of this work is that in a less compact carbonaceous bed, oxygen can diffuse into the bed from the top or any other section which is in direct contact with air. As the coal ages (reaction rate falls with time) at a given depth, the concentration of oxygen increases with time. Thus as time increases heat will be released at an increased depth where it will be more difficult to lose. As a result heat generation leading to spontaneous combustion even after a long time cannot be ruled out. A more reactive and more compact layer than used in the experiments could initially limit the oxygen penetration even more, but as mentioned before as the coal ages, the oxygen penetration will increase with time so that a reactive layer covering a bed can never be a long term solution for preventing spontaneous combustion.

CHAPTER IV

ISOTHERMAL OXIDATION of COAL

4.0 Experimental techniques

The apparatus used in this experiment is a simpler version of the one used by Smith (1993). The principle employed is basically the same, the few exceptions being that in this dissertation the experiment is volumetric based as compared to the gravimetrically l- one by Smith (1993). The experiment was based on the principle of upward displacement of oil. The absorption of oxygen by coal in the air tight apparatus would lead to the formation of a "vacuum" which would be replaced by oil which was in direct contact with the enclosed air. To compensate for variations likely to be induced by environmental factors such as the variation of atmospheric pressure, a blank was run parallel to each set of test samples. The corrected overall change in volume of the system after a particular period of time was equivalent to the volume of oxygen absorbed by the coal during that period.

4.1 Static Isothermal Oxidation Apparatus

The isothermal oxidation experiments were carried out in modified flat bottomed flasks. The basic structure of the apparatus consisted of a flask with a side valve fitted onto it. This could be used to flush air out of the flask.

A ground glass joint was used to connect each flask to a graduated burette with one of its ends dipped into cooking oil in a beaker. A diagram of the apparatus set-up is shown in fig 4.1 below. As an additional precaution to reduce chances of air leaks, all the ground joints were made air tight by the use of high vacuum grease. The experiments were run in a constant temperature room in which the temperature was thermostatically controlled at about 20°C. The temperature fluctuated between 19 and 21°C.

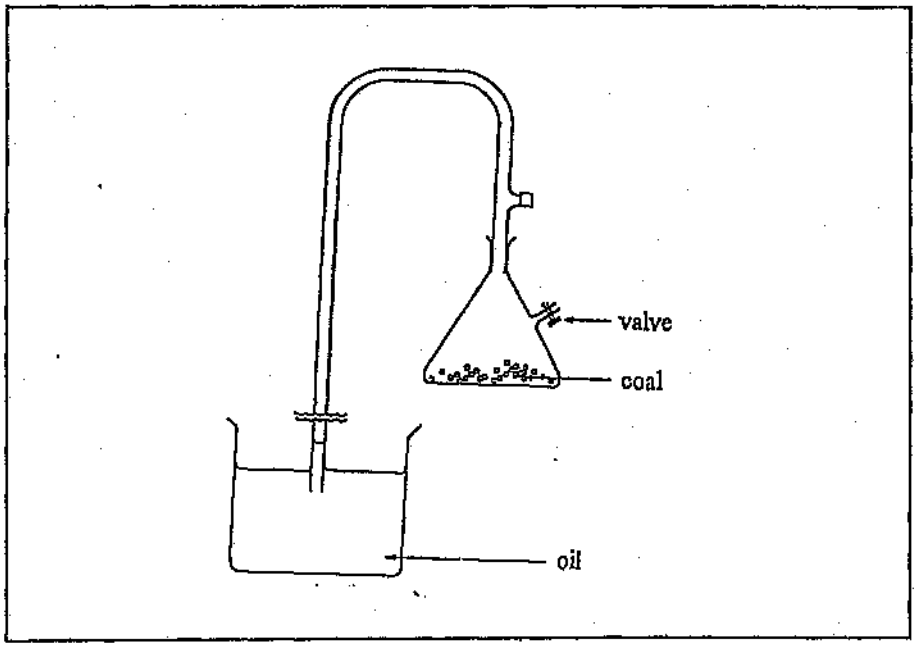


Fig. 4.1 Static Isothermal Oxidation Apparatus.

4.2 Experimental Procedure

The method involves the use of coal of known mass and particle size at a constant temperature. Samples of 20g of coal were weighed and charged into each reaction vessel. For the reaction in 21% oxygen the apparatus was left with an open valve for 20 minutes to stabilise the contents with the surroundings. The procedure was modified slightly for the oxidation in 10%, 50% and 99% oxygen. The apparatus charged with coal was flushed with the respective gas from a cylinder at a flow rate of 360 cm^3/minute for five minutes in each case. The flasks were then allowed to return to ambient pressure by leaving the valve open in an appropriate oxygen concentration environment until there was no pressure difference between the flask contents and the surroundings.

4.3 Results

Fig:4.2 and 4.3 shows the variation in oxygen absorbed with time.

The rate of absorption of oxygen was found to be initially high and then decreased with time. This behaviour was observed in all runs. From the results obtained, it seems like the coal is highly reactive in the region within the

first 30 minutes after which it slows down. This is likely to be due to the fact that the coal is still fresh hence maximum absorption of oxygen. The second type of behaviour observed is an increase in the rate of oxygen uptake with an increase in the initial oxygen concentration. The most likely explanation for this is that the initial stage of the reaction is a "rapid" adsorption process until the "active" sites are saturated.

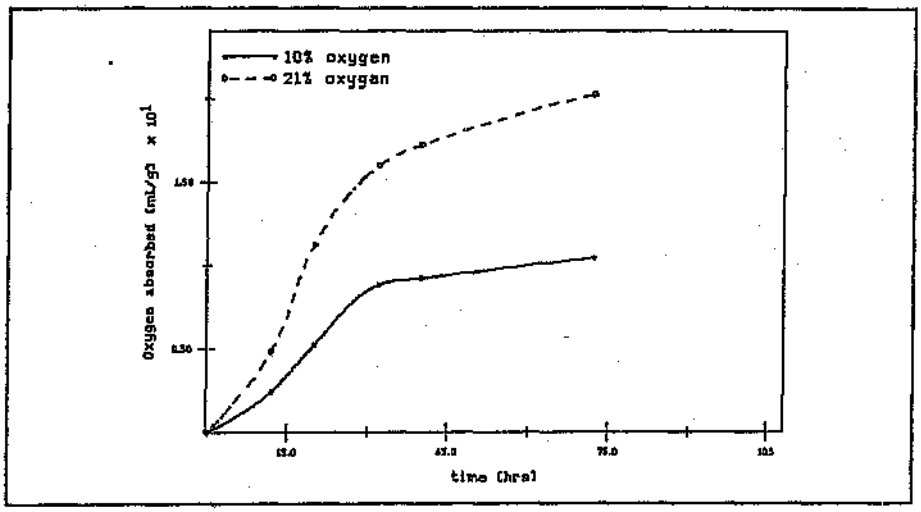


Fig. 4.2 Oxygen absorption in 10 and 21% oxygen

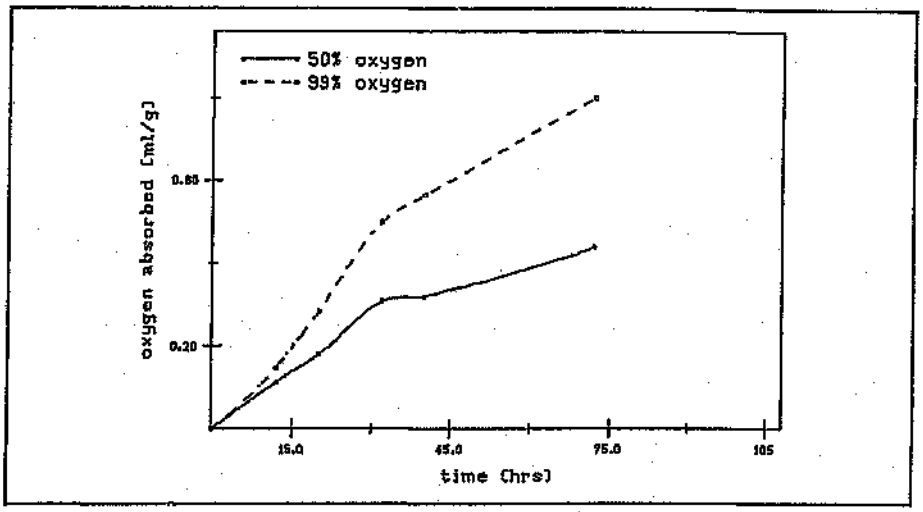


Fig. 4.3 Oxygen absorption in 50 and 99 % oxygen

4.4 Reproducibility of results

To assess the extent of consistency of the results, repeat experimental runs under the same conditions were done and these are plotted for the various concentrations dealt with. Figs:4.4 - 4.7 shows these plots.

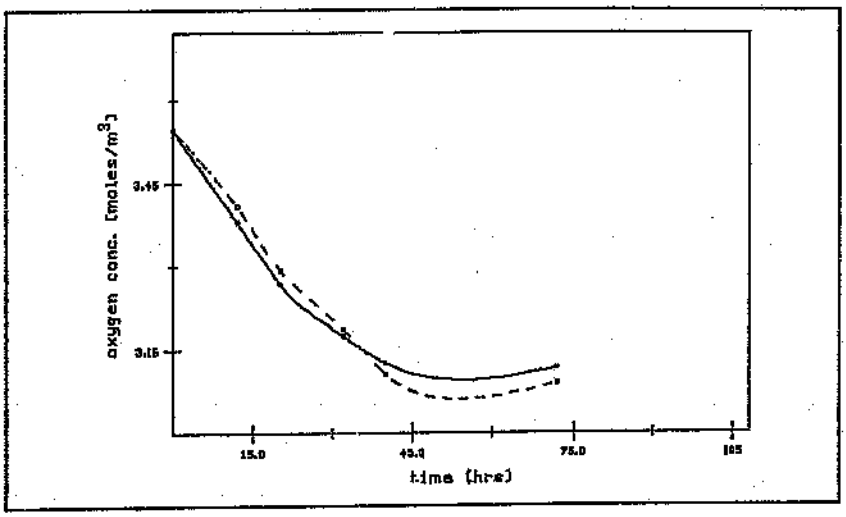


Fig. 4.4 Reproducibility of the 10% oxygen analysis

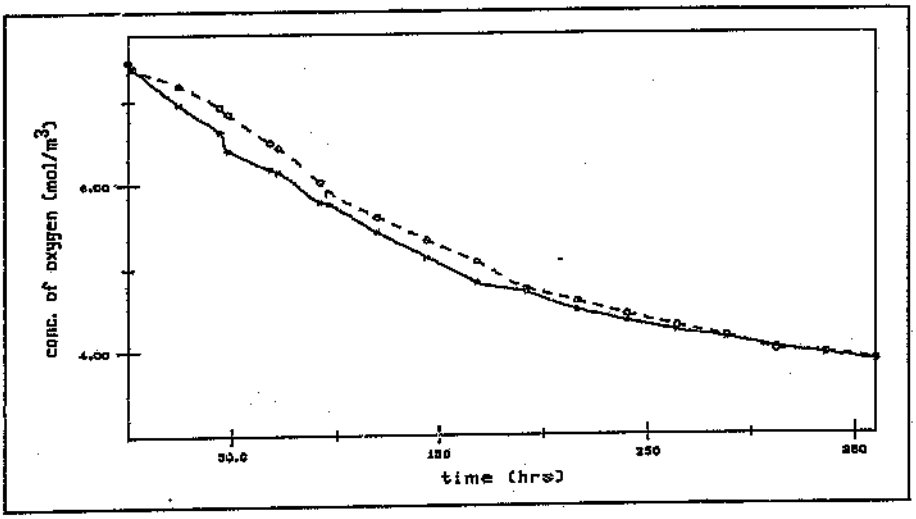


Fig. 4.5 Reproducibility of the 21% oxygen analysis

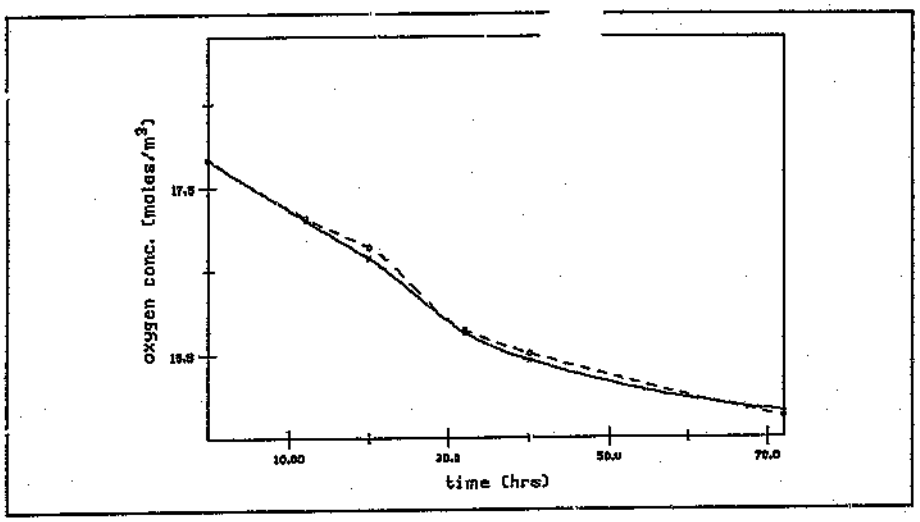


Fig. 4.6 Reproducibility of the 50% oxygen analysis

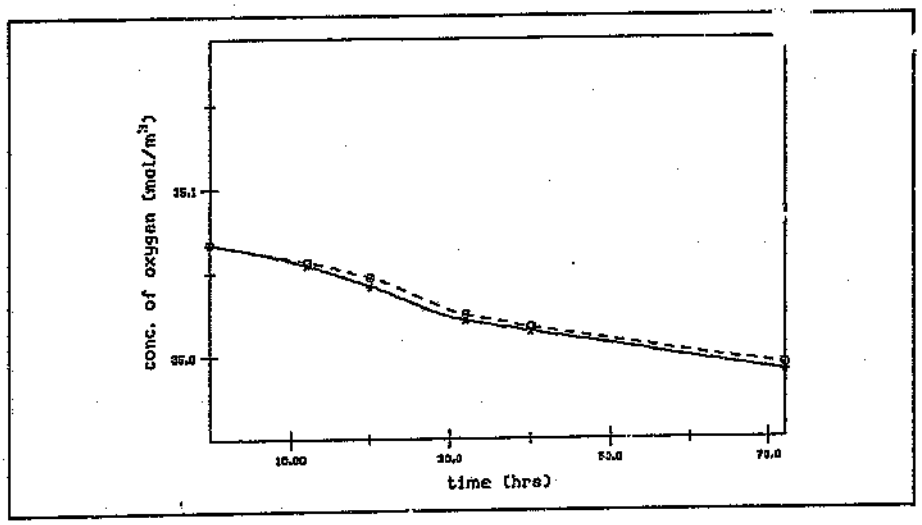


Fig. 4.7 Reproducibility of the 99% oxygen analysis

4.5 Mathematical Modelling

Low temperature oxidation of coal has been investigated by quite a number of people, Smith, (1993), Brooks, (1985), Itay, (1983). The main differences between the various work covered in literature is the temperature of operation. Coal oxidation has been investigated within a temperature range of 20-300°C. One cannot expect the reaction kinetics to be the same within such a vast range of temperature. Obviously temperature is going to play a major role in the oxidation mechanisms involved.

This can be supported by the findings by Smith, (1993), in his model he found out that the reaction at 50-80°C is controlled by macropore diffusion whereas at 23°C there is a mixture of micropore and macropore diffusion. The latter should be the case in this study since the temperature of operation is around 23°C.

Chemisorption of oxygen is the major low-temperature reaction and the rate varies from one sample to another. For the different concentrations of oxygen used, there was an increase in the rate of oxygen uptake with increase in concentration of oxygen.

If we consider what was happening in each reactor during the experimental period, we find out that in cases where there was a higher concentration of oxygen the rate of its consumption was correspondingly high. From this observation we can try to establish a relationship between the initial reaction rates and the initial concentrations of oxygen in the reactors.

We can now determine the reaction order with respect to the oxygen concentration. This can be done if we make the following assumptions:

(a) There is no pre-oxidation of the coal samples.
(b) Initial concentration of oxygen in the flasks is that of the gas used.
(c) There has been no temperature or pressure change.
(d) The coal reactivity decays with time.
(e) Volume of oil sucked up in the burette is equal to volume of oxygen absorbed.

4.6 Model Equation

The rate of reaction for the coal in the reactors can be represented in a form slightly modified from that proposed by Itay (1983) which can be summarised as given below:

$$\frac{dC}{dt} = r = \frac{C^n}{1 + k(C_o - C)} \qquad [4.1]$$

Where: C_o is initial concentration of oxygen

C is concentration of oxygen at time (t)

n is order of reaction

k is a constant

The value of the oxygen concentration, which is present in excess, does not change much in the initial stages of the reaction. Thus $C = C_o$, at the initial conditions of the reaction. We can therefore write an expression for the initial rate, if we assume an n^{th} order reaction rate which is given below.

$$r_i = C_i^n \qquad [4.2]$$

If we had the initial rates we could in principle determine the order of the reaction, n by plotting the logarithm of r_i vs C_i.

$$\ln(r_i) = n\ln(C_i) \qquad [4.3]$$

However it is quite difficult to estimate the initial rates as at this stage the initial transient effects are still settling down. However equation 4.1 can be integrated with the assumption that the overall gas phase concentration for each run does not vary much with time, ie C^n is effectively a constant for each of the runs with different initial concentration. However the ageing effects are largest at the start of a run and it is probably not a good assumption to let $C - C_o$ be zero. By integrating equation 4.1 with these assumptions we can obtain the result that t can be expressed as a quadratic in C. The best way to determine the initial rate is to use a graphical method.

The initial rate method was used to establish the order of the reaction, n. The basis of the method being to measure the rate of the reaction over a period of time short enough for the reaction not to have proceeded significantly. Reaction rates for the four different concentrations can be obtained from plotting time versus moles of oxygen absorbed. Using the best fit method, constants for a second order polynomial function can be generated for each run.

The polynomial function given can be written as:

$$t = bNo_2 + cNo_2^2$$

Where: t is time

No_2 is number of moles of oxygen absorbed

b is $1/r_i$

c is a constant

Since b is $1/r_i$, hence its inverse will give the initial rate of the reaction. A plot of time/moles absorbed versus moles absorbed can be used as an alternative to the one above (the straight line graphs at the top of graph). In this case a first order polynomial function of the form $t/No_2 = b + CNo_2$ is obtained. For all the graphs the initial rate of oxygen absorption, b should be the same as that obtained from the corresponding second order polynomial function. Figs. 4.8 to 4.11 shows the plots of different concentrations of oxygen from which the values of b were worked out.

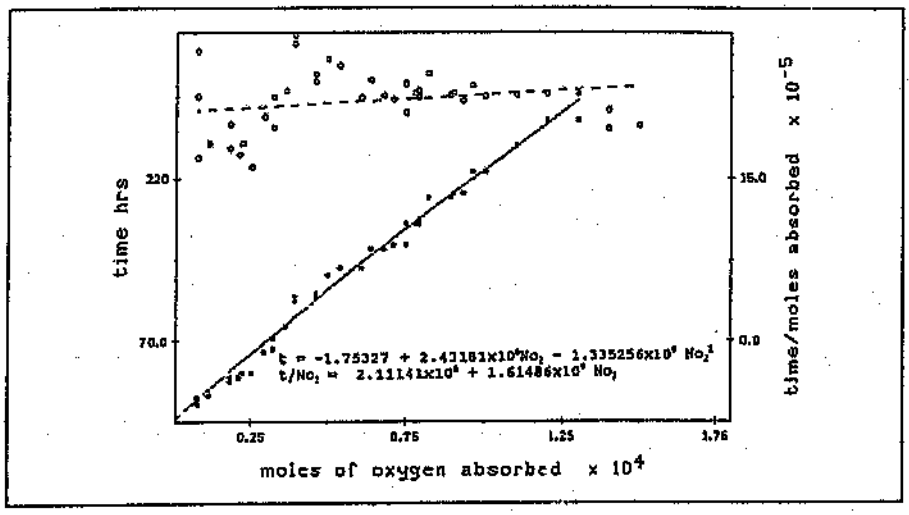


Fig. 4.8 Determination of initial rate for 10% oxidation

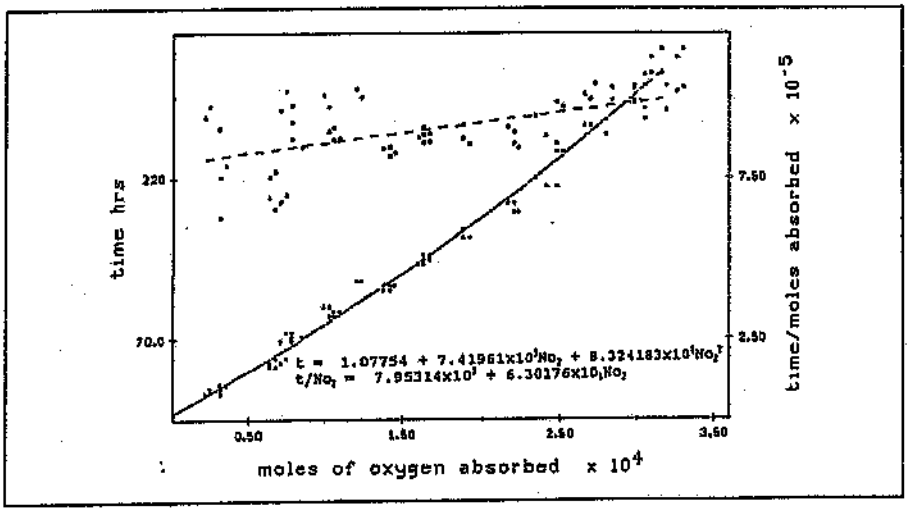


Fig. 4.9 Determination of the initial rate for 21% oxidation

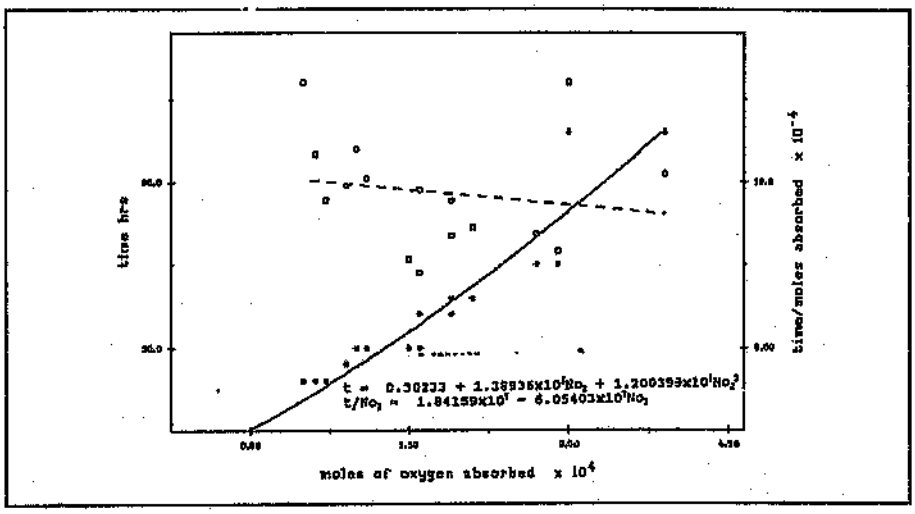


Fig. 4.10 Determination of the initial rate for 50% oxidation

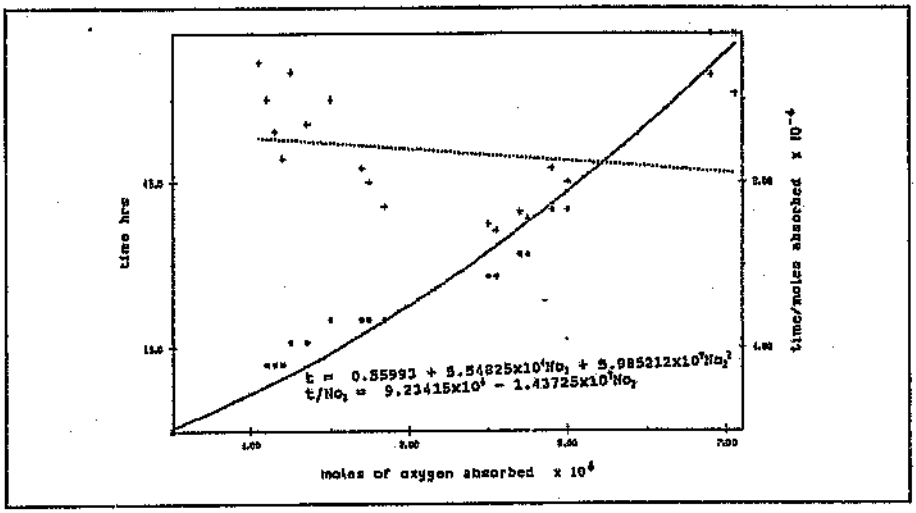


Fig. 4.11 Determination of the initial rate for the 99% oxidation

On the graph of time versus moles of oxygen absorbed a second y-axis can be added whose values are calculated from the product of time and inverse moles absorbed. A straight line graph generated from the second y-axis versus the moles of oxygen absorbed data should also give a slope equal to the inverse of the initial rate of reaction (r_i). The data for the four different concentrations can be treated in the above mentioned manner and corresponding initial rates can then be worked out. The quadratic equation is likely to give a better value of b since it is a direct plot of concentration vs time. The points are not all that scattered as compared to the first order polynomial determination.

Once we have these initial rates, a plot of $\ln r_i$ versus $\ln C_o$ should yield a straight line of gradient n, if we can assume power law kinetics. Thus a plot of ln(1/b) versus $\ln[O_2]$, at the initial conditions for each run should give a straight line whose gradient is the order of the reaction. The graph is given in Fig. 4.12 below. A slope of 0.807 was obtained which compares fairly well with the findings given in literature where Smith (1993) and Itay (1983) found slopes in the order of 0.57. Kersner (1980), found slopes ranging from 0.4 - 1.0 .

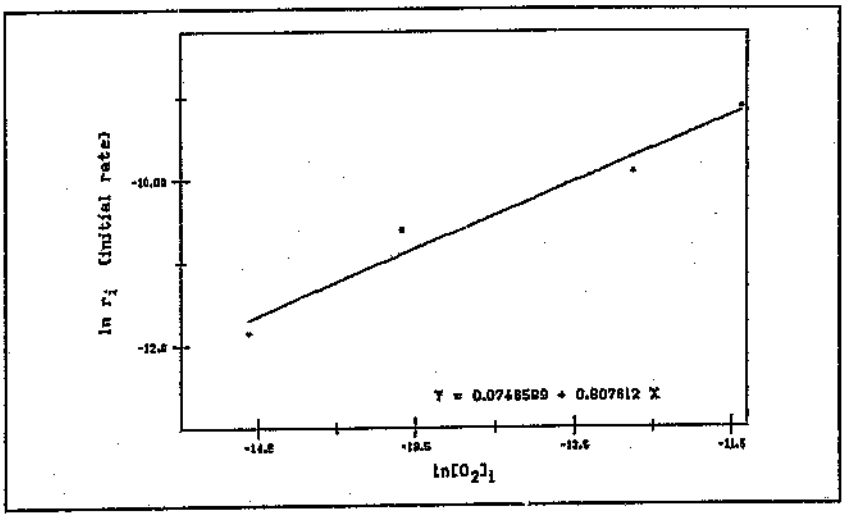


Fig. 4.12 Determination of the order of reaction

4.8 Conclusions

The mathematical modelling of the data yielded results consistent with the general findings for the low temperature oxidation of coal. Fractional orders of reaction with respect to oxygen concentration were also obtained in the work by Smith (1993) and also by Itay (1983).

The main step in the low temperature coal oxidation is the absorption of oxygen. The consumption of oxygen was found to initially proceed at an appreciable rate which then

slowed down with time. This is evidence of the "ageing" effect of the oxidation of coal. The major coal - oxygen reaction at low temperature is thought to be absorption of oxygen. There was no carbon dioxide detected despite the reasonable reduction in the oxygen concentration observed in all four runs at different concentrations, thus confirming this result.

The fact that the result of oxygen absorption versus time are well - fitted by a quadratic confirms that the model equation of Itay (1983) is a reasonable method for modelling coal oxidation as a function of time.

CHAPTER V

DRYING OF COAL UNDER NITROGEN

5.0 Experimental techniques

The rate of loss of moisture was investigated using dry oxygen-free nitrogen at a flow rate of 380cm^3 /min. This is one of the methods recommended by the British Standards Board. Though this method is normally used for coarsely crushed coal, it was found to be applicable to relatively thin plates of coal.

Prior to choosing this method some constraints and limitations of thermal methods were considered and it was decided it would be difficult to differentiate between naturally occurring moisture and water produced as a result of chemical reaction. However, with the method used one is assured of only getting moisture which is initially present in a coal sample.

5.1 Coal Drying Experimental Apparatus

The equipment used consisted of 4 main units, a gas supply from a cylinder fitted with a regulator and a flow meter, a balance, a gas drying tube containing anhydrous copper sulphate and a modified test tube to hold the coal block. The apparatus was linked through a system of polythene tubes, ground joints and tapes. Ground glass joints were used for easy removal of the test tube holding the sample so that it could easily be

weighed and the taps were used to separate the contents of the tube from the ambient air. A diagram of the complete apparatus is shown in figure 5.1 below

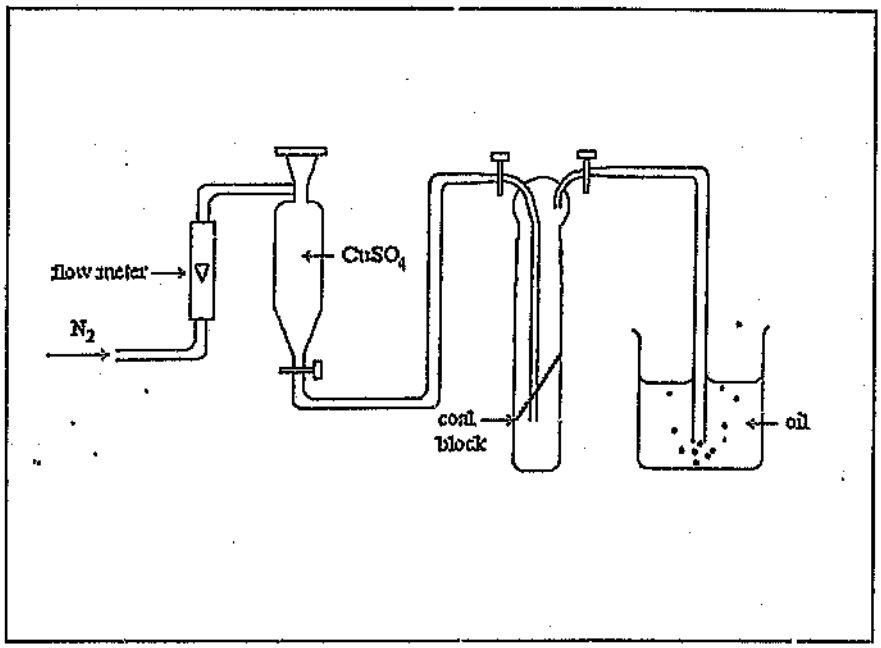


Fig. 5.1 Coal drying apparatus

5.2 Measuring procedures

A block of coal of known mass and area was placed into the drying vessel which was weighed again. High purity nitrogen was then continuously passed through the drying tube. The nitrogen was regulated to a pressure of 500 kPa and a flow race of 380cm^3/min, to make sure that the

nitrogen was dry enough it was passed through a tube containing anhydrous copper sulphate before being passed through the tube containing the coal sample. The tube containing the sample was removed and weighed at given time intervals until a constant mass was finally obtained.

5.3 Results

The experiments carried out exhibited results which follow a systematic pattern. Initially there is a rapid loss of moisture which gradually falls until there is no further loss of moisture. The behaviour exhibited by the coal blocks can be best explained by two mechanisms i.e., the shrinking core type of reaction or a bound water type of reaction. These are explained in more detail in section 5.5.0. Some of the drying results are shown in Figs. 5.2 and 5.3 below. The R-squarad value was used to evaluate the reliability of each trend line, this was done using microsoft excel. Results obtained are shown in Appendix C and Appendix D. Besides runs 7 and 13 the results are fairly reliable.

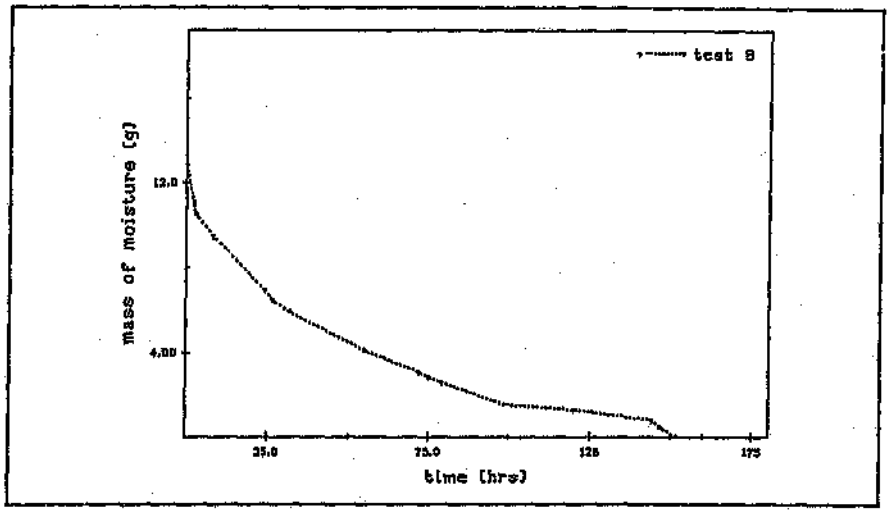


Fig. 5.2 Typical drying run

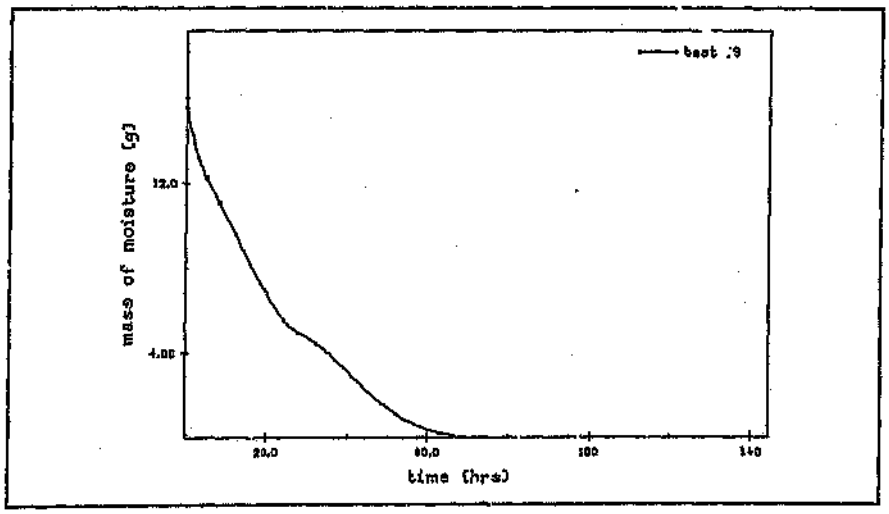


Fig. 5.3 Typical drying run

5.4 Reproducibility of results

The same conditions were applied to all the samples during the drying process. One problem was that it was not possible to cut out coal blocks which were exactly of the same dimensions from the "parent" block. Added to this the heterogenous nature of the coal would also make the results variable. There was thus a need to verify how meaningful the results were. The reproducibility of the drying process was tested and results are shown in fig: 5.4 and 5.5. The reproducibility for test 6 and 7 is poor,. However for test 3 and 4, the reproducibility was better.

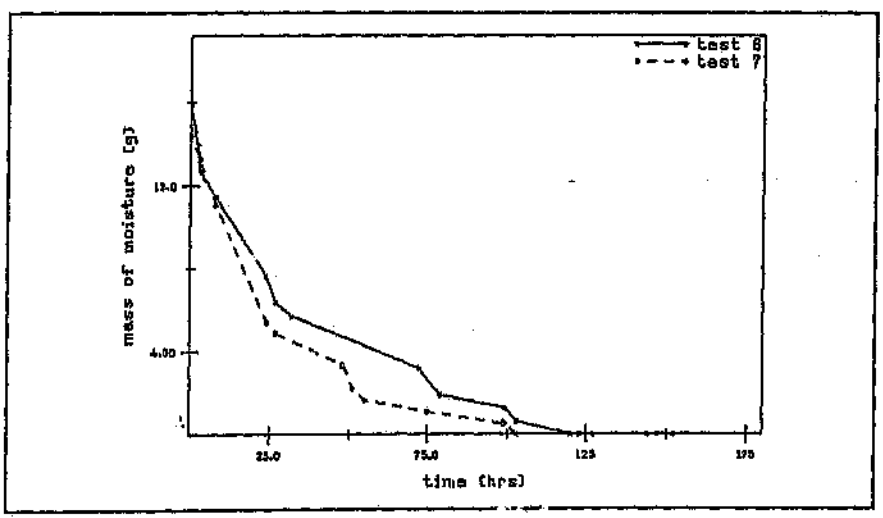


Fig. 5.4 Reproducibility of the drying results

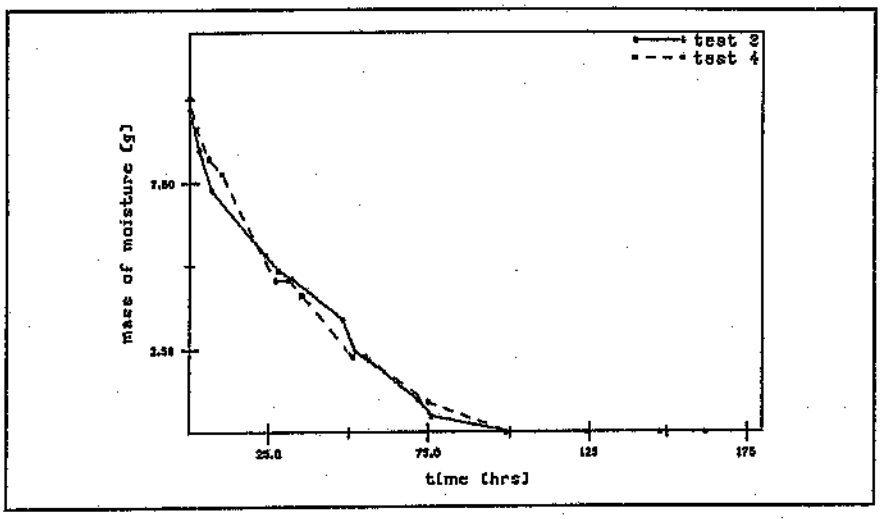


Fig. 5.5 Reproducibility of the drying results

5.5.0 Mathematical Modelling

Moisture has been found to play a vital role in the oxidation of coal, as a result the study of coal drying has been run in parallel to that of quantifying and assessing the effect of moisture on coal oxidation in general.

However there is a problem of studying drying and oxidation together. The solution we have chose is to minimise the oxidation by the use of low temperatures and inert gases for the drying process. This will then justify our assumption that the change in mass of the coal block is due to moisture loss only. Simple reaction

kinetics expressions can then be worked out. The reaction order of drying has been found to be one with respect to concentration of reactive sites by some researchers, Karsner, (1980).

There are two simple possible ways the drying mechanism can be modelled. One of the possibilities is the shrinking core mechanism. In brief it can be summarised as follows, as the coal dries up the moisture "rich" section of the coal becomes separated from the flowing dry nitrogen by a dry layer in the coal. The moisture has then to diffuse through this layer. However cracking of the coal blocks leads to exposure of new moisture rich surfaces and there is thus a tendency for the coal to release more moisture than expected due to the opening up of water containing sections of the coal.
The other possibility is the bound water approach, where the water is regarded as being absorbed and its vapour pressure plays a significant role.

Thus one has some sort of isotherm between the bound water and the vapour. The following general assumptions will be made for the two mathematical models in this study:

(a) The coal block is two dimensional and loss of moisture is through a single pair of surface.

(b) No volatile or oxidation products are given off during the drying process.

(c) There are no temperature effects, as the temperature is kept constant throughout the drying period.

5.5.1 Bound Water Model

In this case we assume the water is absorbed into the coal and the coal exerts its equilibrium vapour pressure which depends on the amount of water still remaining in the coal. We then assume the rate at which the water evaporates is proportional to the vapour pressure difference between the coal and the air. If the air is completely dry we can therefore write.

$$\frac{dg}{dt} = kp \qquad [5.1]$$

Where: g is the moisture content of the coal

t is time (t)

k is a constant

p is the equilibrium vapour pressure of the wet coal.

Now if we assume a Henry's Law isotherm we have that:

$$p = gH \qquad [5.2]$$

Where H is the Henry's Law constant

$$\therefore \frac{dg}{dt} = gHK \qquad [5.3]$$

Where $g = g^{\circ}$ at $t = 0$

Integrating the above equation gives the solution given below:

$$g = g^{\circ}\exp(-HKt) \qquad [5.4]$$

If this model is valid, a plot of the natural log of the mass of moisture, ln(g) versus time (t) should yield a straight line with a slope -KH and intercept $\ln(gC^{\circ})$.

5.5.2 Fitting the mathematical model to the results

A reasonable straight line has been obtained in each case as shown in Fig. 5.6, the values of -KH and g°.were estimated. The values obtained are given below, in Table 5.1.

Table 5.1 Values of g° and -KH

test	g°	-KH
6	14.50	-0.02
7	12.43	-0.03
8	13.91	-0.02
9	13.44	-0.03

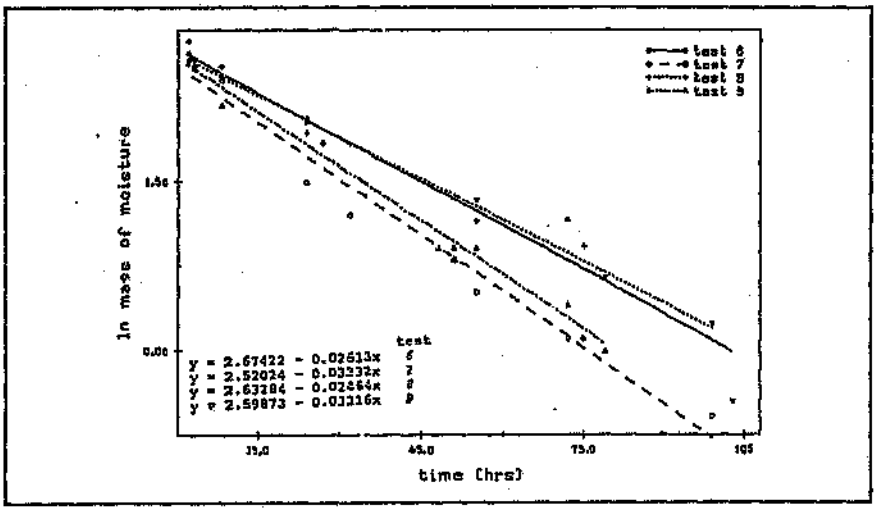


Fig. 5.6 Testing the bound water model

The best fit of the model for the four tests is shown in Figs. 5.7-5.10 given below.

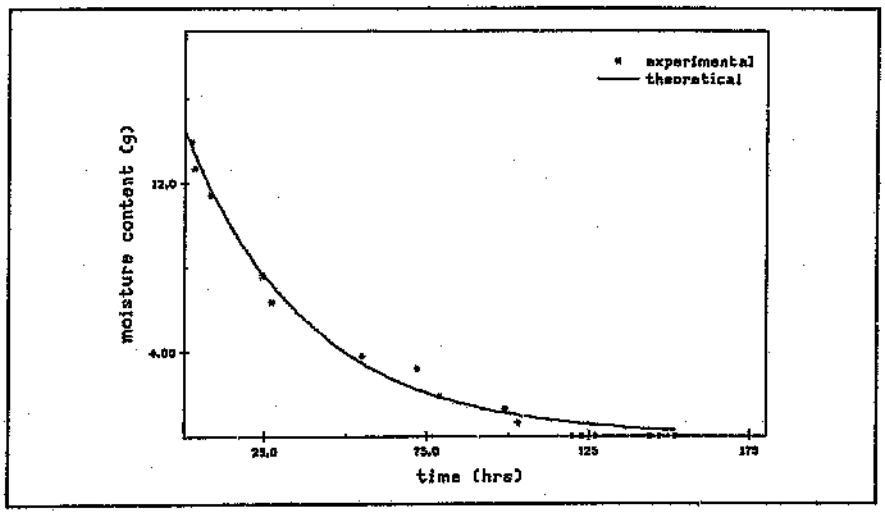


Fig. 5.7 Mathematical model fit for run 6

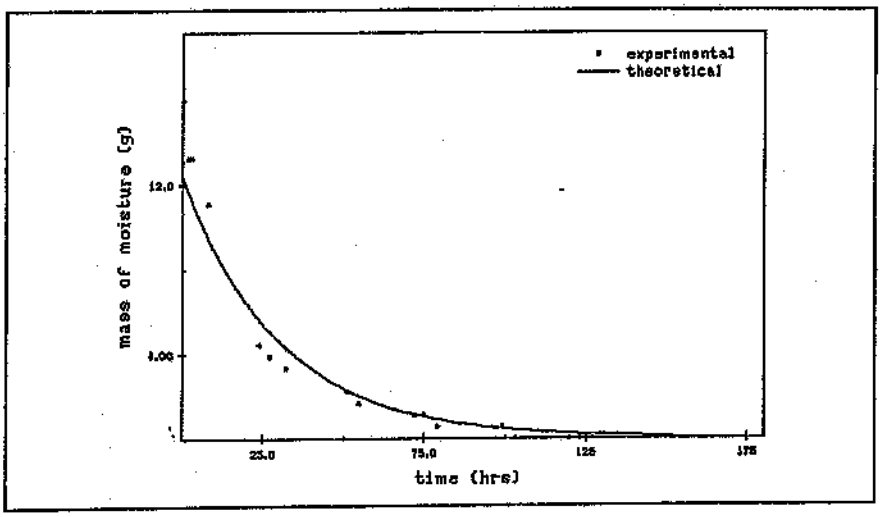


Fig. 5.8 Mathematical model fit for run 7

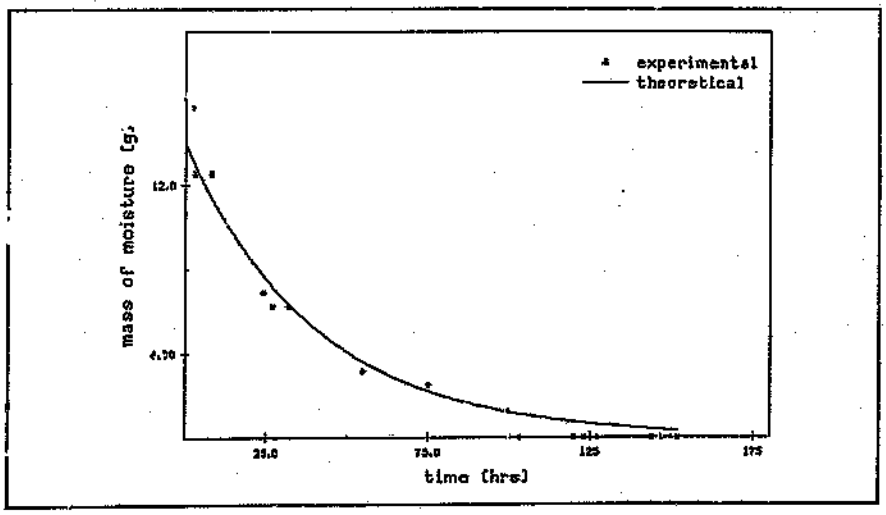


Fig. 5.9 Mathematical model fit for run 8

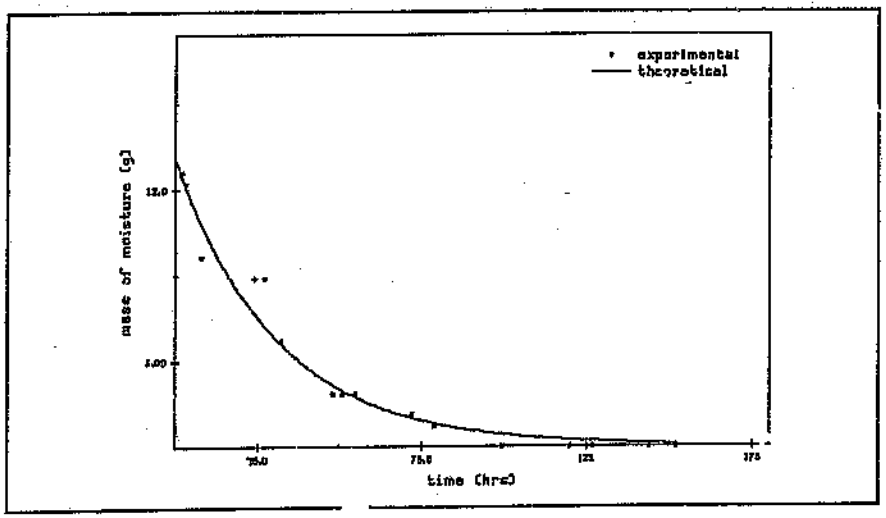


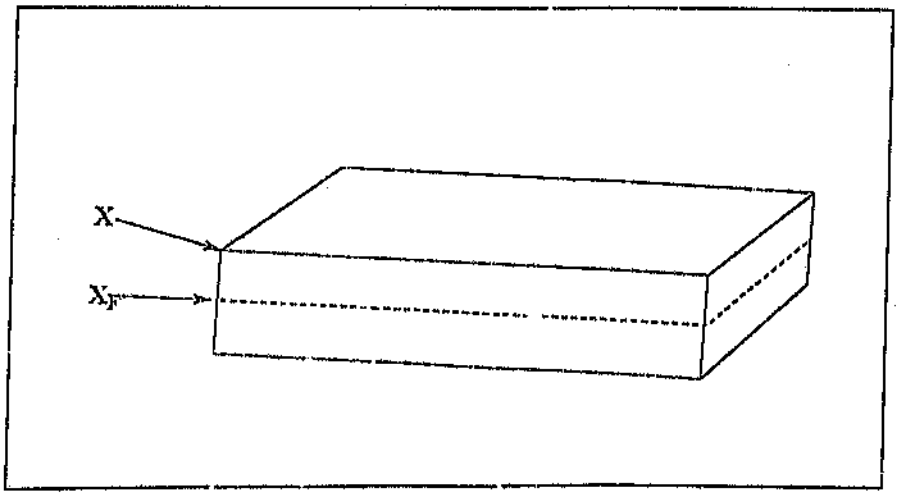
Fig. 5.10 Mathematical model fit for run 9

5.5.3 Shrinking Core Model

Alternatively it might be that the water effectively is absorbed into the lattice like in a sponge and that it merely evaporates from the surface. As this layer of water in the coal shrinks the remaining water has to diffuse through the coal layer to get to the surface and

can assume that this layer acts as a diffusional
istance to evaporation. Because of the large density difference between gaseous and liquid water it is reasonable to suggest that we can assume the gas phase sets up a pseudo- steady state concentration profile.

Thus we can write using Fick's Law when the thickness of the layer of coal between the surface and the evaporating front is X :



$$D\frac{d^2c}{dx^2} = 0 \qquad [5.5]$$

Where x is the depth in the dry layer from the surface.

$$\therefore\ c = Ax + B \qquad [5.6]$$

Now c = 0 at x = 0 (air has no moisture)

and c = c^o at x = X

$$\therefore\ c = c^o\frac{x}{X} \qquad [5.7]$$

Where c^o is the concentration of water vapour in equilibrium with liquid water at the temperature of the experiment.

Now that we can say that the rate of loss of moisture is equal to the flux of water at the surface.

$$\frac{dg}{dt} = -D\frac{\partial c}{\partial x}\Big|x = 0 \qquad [5.8]$$

$$= -\frac{c^o}{X} \qquad [5.9]$$

The thickness of the remaining water layer is given by $X - X^F$. The fraction of the water left is given by the equation below:

$$\frac{g}{g^o} = X^F - \frac{X}{X^F} \qquad [5.10]$$

Where: g^o is the initial moisture content of the coal

X^F is the thickness of the coal specimen.

$$\therefore \frac{dg}{dt} = \frac{+c^o}{(g^o - g)} \frac{g^o}{X^F} \qquad [5.11]$$

$$Let\ y = \frac{g^o - g}{g^o} \quad \therefore g = g^o(1 - y) \qquad [5.12]$$

$$dg = -g^o dy \qquad [5.13]$$

$$\therefore \frac{dy}{dt} = \frac{c^o}{yX^F g^o} \qquad [5.14]$$

$$\therefore \frac{1}{2}y^2 = \frac{c^o}{X^F} g^o t + F \qquad [5.15]$$

Now y = 0 when g = 0 at t = 0

$$\therefore F = 0$$

$$\therefore y^2 = \frac{2c^o}{X^F g^o} t \qquad [5.16]$$

$$\therefore (g^o - g)^2 = \frac{2c^o g^o}{X^F} t \qquad [5.17]$$

A graph of $(g^o - g)^2$ or y^2 vs time (t) given below was plotted to test the validity of the experimental data. Thus the plot should give a straight line going through the origin if the data is compatible with the model. This has been found to be the case as shown in fig.5.6 below, one important observation is that the line is straight up to the point at which the coal is completely dry which occurs when y = 1 or g = 0.

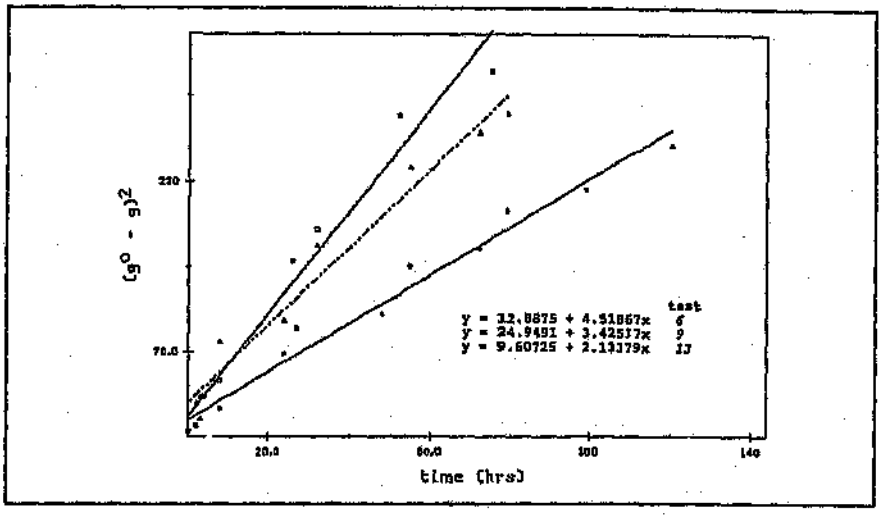


Fig. 5.11 Testing the shrinking core drying model

5.5.4 Fitting the mathematical model to the results

Values of g° and $c^\circ g^\circ/X^F$ were estimated from the above graph using linear least square and the values are given in the table below.

Table 5.2 Values of g° and $c^\circ g^\circ/X^F$

test	g°	$c^\circ g^\circ/X^F$
6	11.20	2.23
9	23.81	3.52
13	5.28	5.30

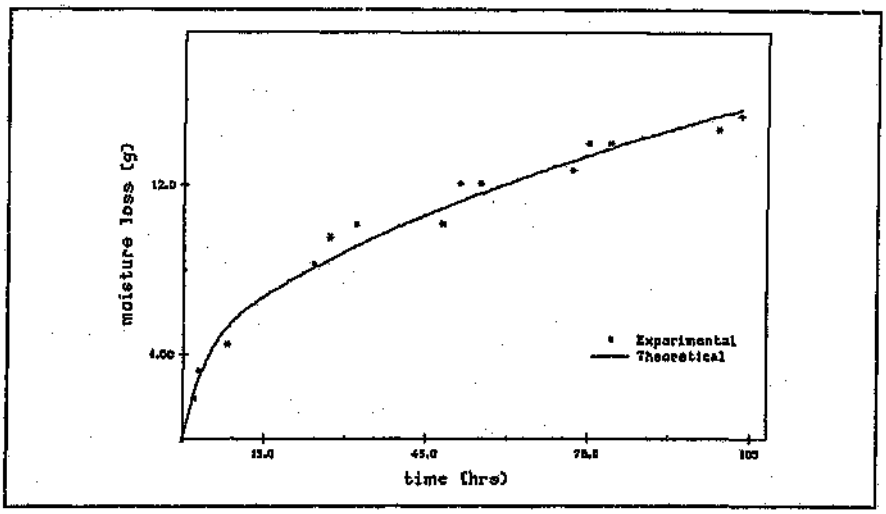


Fig. 5.12 Fitting for run 6

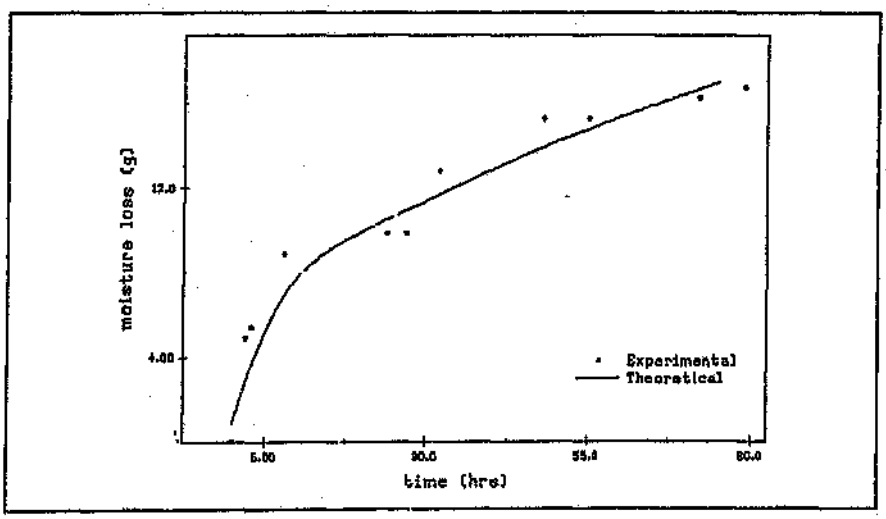


Fig. 5.13 Fitting for run 9

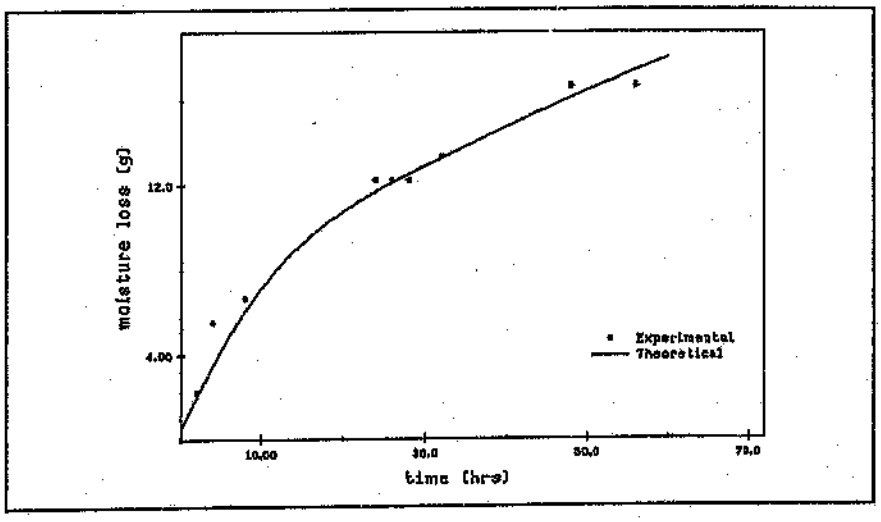


Fig. 5.14 Fitting for run 13

5.6 Conclusions

Two possible drying models have been tested in this work, to determine the amount of moisture in a coal block as a function of time. The method used to determine the moisture has an advantage over the thermal based methods in that there is negligible oxidation and no heating is involved.

The results show that the rate of moisture loss falls with time until a point is reached where there is no further loss of moisture.

The shrinking core model suggests that the water

evaporates from the surface of the coal and as the water layer shrinks, the remaining water has to diffuse through the coal layer to get to the surface. Th bound water model is based on vapour pressure difference between the coal and the dry air

Both models were tested and reasonable straight lines were found in both cases, the points for the shrinking core model are more scattered and the fit is not that good especially in the initial stages of the experiment. The fits in the bound water model are h better than those of the shrinking core model.

However the results certainly suggest that the weight goes to a fixed value after a finite time rather than asymptote to a final value. This suggests a shrinking core type model. In order to try to decide which of these two models is best will require more work. Perhaps cutting open a piece of coal after partial drying might, if there is a visual difference between moist and dry coal, provide a way of deciding if the shrinking core model is reasonable. Possibly of course these two models are too simple and one might require a more complex model.

CHAPTER VI

CONCLUSIONS

In this dissertation the author has looked at a number of simple experiments which relate to coal oxidation and drying. Simple models have been reasonably successful in describing the results. The results and the models could prove to be useful in trying to describe the behaviour of real coal and waste material dumps where both oxidation and drying occur simultaneously.

Though the coal has been from the same mine the different prior treatment before the onset of the experiments, that is drying in the case of the column fed coal, grinding for the isothermal reaction experiments coal and cutting for the drying coal makes it a bit difficult to convincingly relate the findings in the three experiments.

The diffusion experiment could prove to be a useful technique for assessing the rate of reaction of coal samples or waste material with oxygen. This is because the material could be used as is without for instance crushing or drying.

The pipe was in an open space (it could even be put outside) which resembles the natural environment in which coal dumps and piles are exposed. This might prove to be a useful asset in obtaining information which could be valuable in the management of waste dumps or coal storage

dumps. It provides a reasonable approximation of the rate of the coal reaction with oxygen and the general oxygen concentration profile and the way in which it changes with time can be used to assess the risks associated with a particular dump.

Furthermore one is also able to perform long term experiments and hence get an estimate of the ageing of the material as it reacts with oxygen as well as its long term capacity for oxygen absorption. One of the apparatus for protecting a dump at risk has been to provide it with a reactive skin which would effectively remove all the oxygen close to the surface. The apparatus would also be suitable for assessing the usefulness of different materials, their particle size, the thickness of the layer and degree of compaction as a reactive skin on a real dump.

The isothermal experiment is more of a laboratory type of tool where different samples can be compared under standard conditions and the effect of such parameters as oxygen concentration and moisture content can be studied. It also provides a very useful tool for doing quick experiments on small samples such as might be taken from borehole cores.

Clearly the two methods while both being simple and easy

to do complement each other in the bids of information that can be obtained.

It is well known that moisture content can have a large effect on oxidation rates. In reality of course the coal in a real dump is changing its moisture content with time. Thus in order to really predict how the rate of oxidation changes with time we need to also know how the moisture content changes with time and preferably be able to model this. In this thesis an attempt has been made to do such requirements. The results were however not such that the autnor was able to distinguish between two different possible models.

In conclusion the work in this thesis has looked at a number of areas relating to the measurements that need to be done in order to obtain models and parameter values required for assessing the risk of spontaneous combustion in beds of coal and carbonaceous waste.

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Appendix A1

Callibration of the gas chromatograph using air

The gas chromatograph was calibrated by the calculation for the response factor of oxygen from peaks generated by air samples of volume 0.2 - 1.0 ml.Below is the analytical data of air used for the response factor calculations. A denotes peak area, eg AN_2 denotes peak area of nitrogen. f is the response factor.

Air(ml)	AO_2	AN_2	TOTAL A	f
0.2	3462.7	15226	18688.7	0.8555
"	3464.7	15210	18674.7	0.8569
"	3357.6	14474	18688.7	0.8726
0.4	8101.6	35693	43794.6	0.8538
"	6669.3	29030	35699.3	0.8643
"	6742.0	28996	35738.0	0.8747
0.6	8942.3	39616	48558.3	0.8491
"	10419	45976	56395.0	0.8525
"	10408	45951	56359.0	0.8520
0.8	13505	59752	73257.0	0.8502
"	12400	48100	60501	0.8052
"	14200	60401	74601	0.8513

Air(ml)	AO_2	AN_2	TOTAL A	f
1.0	14986	66613	81599.0	0.8463
"	8994.8	39979	48973.8	0.8464
"	9048.8	39989	49037.8	0.8513

Average f = 0.8558

Appendix A2

Results for oxygen concentration profile

Run 1

Bed Height (cm)	December	January	February	March
10	3.3	3.8	3.0	7.4
20	3.2	3.8	4.2	7.5
30	3.2	3.7	4.4	7.7
40	3.4	3.7	4.6	8.1
50	3.6	3.9	4.8	8.4
60	3.8	4.1	4.9	8.9
70	4.1	4.5	5.2	9.1
80	4.4	4.9	5.7	9.2
90	4.7	5.3	6.3	9.6
100	5.2	5.7	6.7	9.9
110	5.8	6.1	7.1	10.2
120	6.2	6.8	7.6	10.5
130	6.5	7.2	8.1	11.1
140	7.2	7.6	8.6	11.9
150	7.9	8.7	9.2	12.7
160	8.9	9.8	10.1	13.5
170	9.8	10.9	11.0	14.2
180	10.6	11.3	11.8	14.8
190	11.7	12.3	12.7	15.5
200	12.8	13.2	13.7	16.3

Bed Height (cm)	December	January	February	March
210	14.0	14.1	14.6	17.5
220	14.8	15.0	15.7	18.5
230	15.7	16.4	16.6	18.5
240	16.9	17.6	17.8	19.4
250	18.4	19.2	18.9	20.2
260	20.1	20.5	20.1	20.8
270	21.5	21.8	21.2	21.6
280	22.3	22.6	21.9	21.3
290	22.3	22.6	22.3	21.8

Results for oxygen concentration profile

Run 1

Bed Height (cm)	April	May	June	July
10	10.6	12.4	13.4	14.6
20	10.6	12.4	14.6	14.5
30	10.7	12.4	15.1	14.3
40	10.8	12.1	15.6	13.8
50	11.2	12.5	15.7	13.8
60	11.9	12.8	15.8	13.6
70	12.1	13.2	15.8	14.3
80	12.1	13.0	15.9	13.0
90	12.5	13.2	16.0	13.2
100	13.0	13.5	16.0	13.2
110	13.3	14.0	16.3	14.2
120	13.4	14.6	16.0	14.9
130	13.4	14.4	16.0	14.9
140	13.7	14.9	16.2	14.6
150	14.5	15.9	16.7	15.8
160	15.4	16.9	17.1	15.9
170	16.1	17.2	17.4	15.9
180	16.4	17.2	17.8	16.6
190	16.7	17.5	18.0	16.4
200	17.5	18.0	17.9	16.9
210	18.2	18.4	18.3	17.3

Bed Height (cm)	April	May	June	July
220	18.7	18.8	19.2	18.1
230	20.0	19.7	20.2	18.1
240	20.6	20.1	20.6	18.1
250	21.3	21.0	21.3	20.7
260	21.7	21.4	22.2	20.7
270	22.0	22.1	22.2	20.0
280	22.6	22.4	22.3	20.7
290	22.4	22.5	22.4	21.7

Appendix A3

Results for oxygen concentration profile

Run 2

Bed Height (cm)	November	December	January	February
10	7.6	8.3	9.0	10.9
20	7.7	8.3	8.9	10.9
30	7.7	8.5	8.9	11.2
40	7.7	8.6	8.9	11.2
50	7.8	8.7	9.1	11.3
60	7.9	8.8	9.4	11.5
70	7.9	8.9	9.8	11.9
80	7.8	8.9	9.9	12.2
90	7.8	9.0	10.2	12.3
100	7.9	9.4	10.2	12.5
110	7.9	9.6	10.4	12.7
120	8.1	9.8	10.6	13.4
130	8.4	9.9	10.7	13.8
140	8.8	10.2	11.1	14.2
150	9.1	10.3	11.3	14.7
160	9.5	10.8	11.4	14.9
170	10.3	11.6	12.3	15.0
180	10.8	12.5	13.2	15.3
190	11.6	13.0	14.2	16.3
200	12.4	14.4	15.2	16.7

continued overleaf...

Bed Height (cm)	November	December	January	February
210	13.2	15.3	16.1	16.8
220	14.6	16.2	16.7	17.6
230	15.7	17.1	17.0	18.5
240	16.1	17.8	17.6	18.8
250	17.6	18.6	18.4	19.1
260	18.3	19.2	19.3	19.4
270	19.0	19.9	20.0	19.8
280	19.8	20.1	20.7	20.8
290	20.7	21.2	21.4	21.2

Results for oxygen concentration profile

Run 2

Bed Height (cm)	March	April	May
10	14.9	16.8	16. 4
20	14.9	16.7	16.4
30	14.9	16.7	16.4
40	14.8	16.8	16.6
50	14.7	16.7	16.8
60	14	16.8	17.0
70	14.7	16.9	17.1
80	14.9	17.1	17.1
90	14.9	17.3	17.2
100	15.2	17.4	17.2
110	15.4	17 6	17.3
120	15.7	17.8	17.5
130	16.09	17.9	17.9
140	16.3	18.1	18.4
150	16.4	18.4	18.9
160	16.6	19.0	19.1
170	16.8	19.9	19.2
180	17.2	19.9	19.4
190	17.6	20.1	19.5
200	18.1	20.3	19.6
210	18.4	20.6	19.6
220	19.0	20.7	19.8

continued overleaf...

Bed Height (cm)	March	April	May
230	19.4	20.8	19.8
240	20.0	20.9	20.1
250	20.5	21.1	20.4
260	21.0	21.3	21.1
270	21.4	21.9	21.5
280	21.9	22.1	21.8
290	22.2	22.3	21.9

Appendix A4

Fittings for oxidation reactions in chapter three.

RUN 1

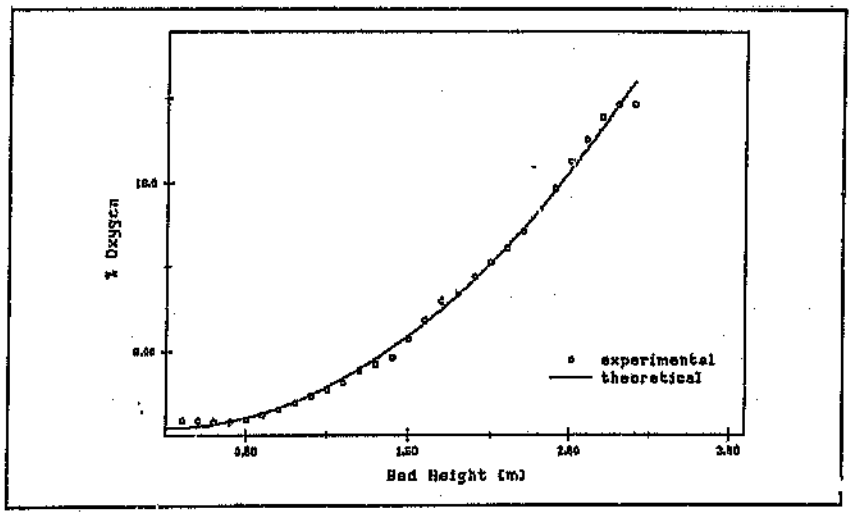


Fig.A.3.1 Fitting for oxygen profile for January 1995

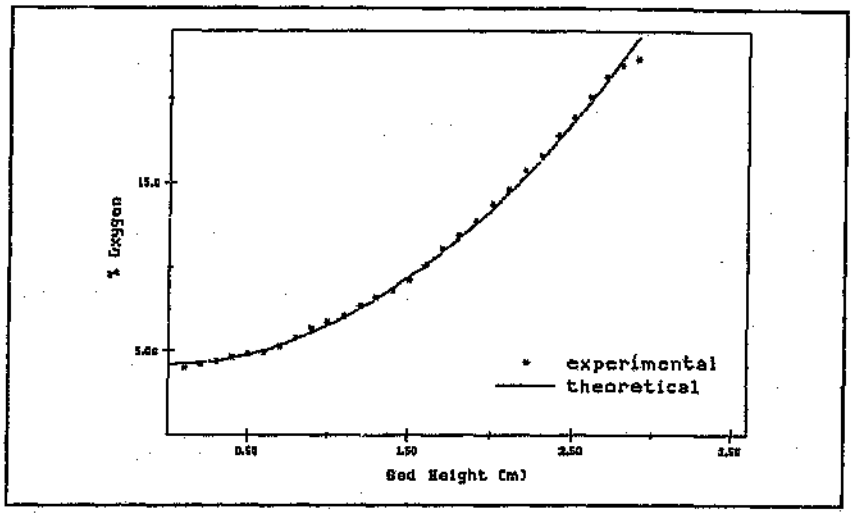


Fig.A.3.2 Fitting for oxygen profile for February 1995

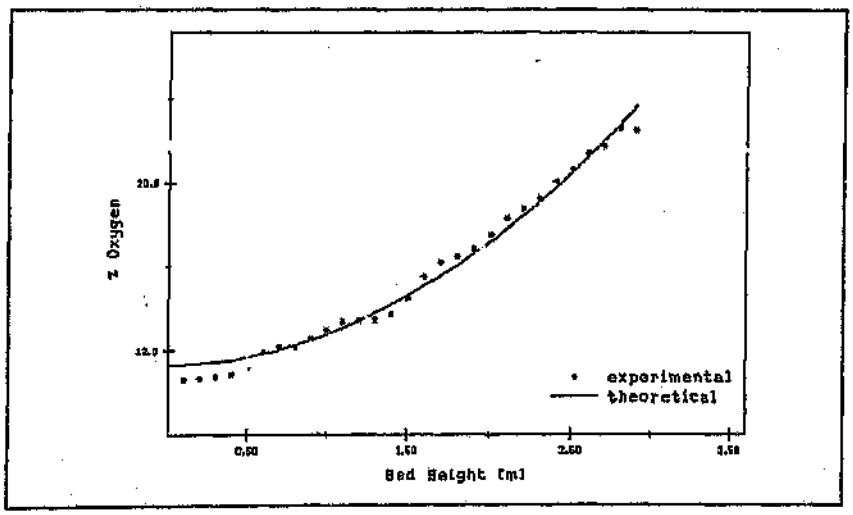


Fig.A.3.3 Fitting for oxygen profile for April 1995

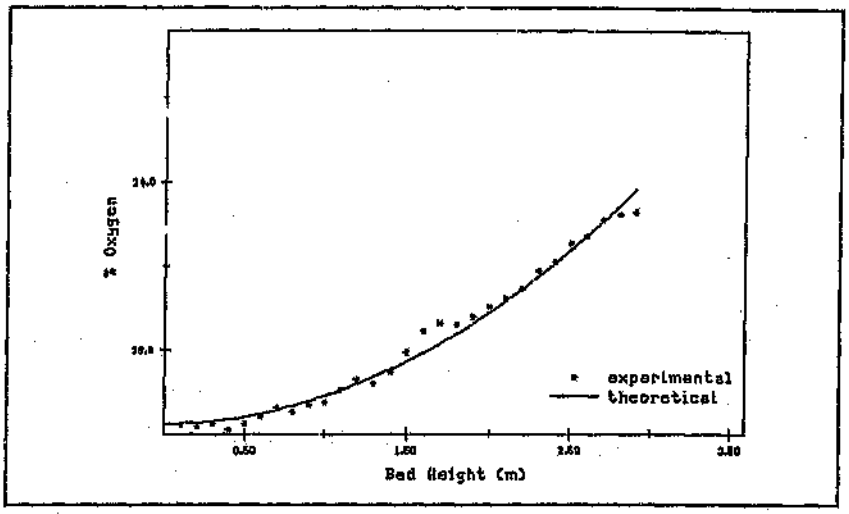


Fig.A.3.4 Fitting for oxygen profile for May 1995

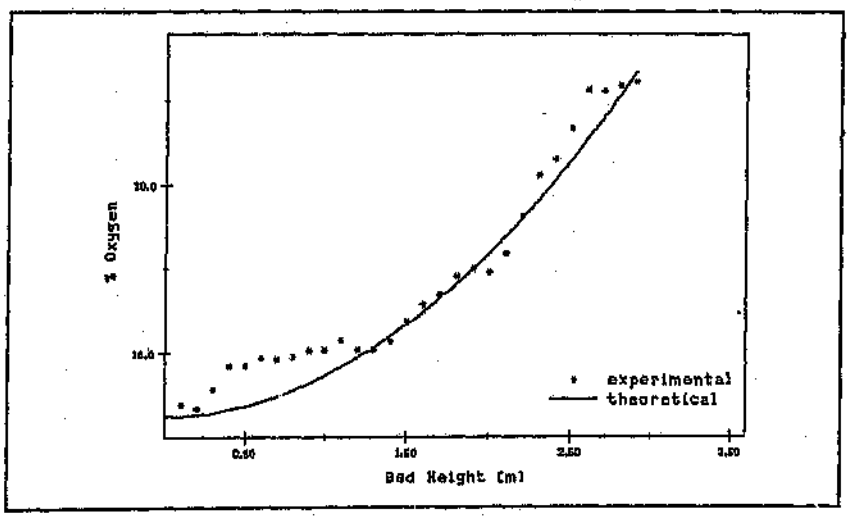


Fig.A.3.5 Fitting for oxygen profile for June 1995

RUN 2

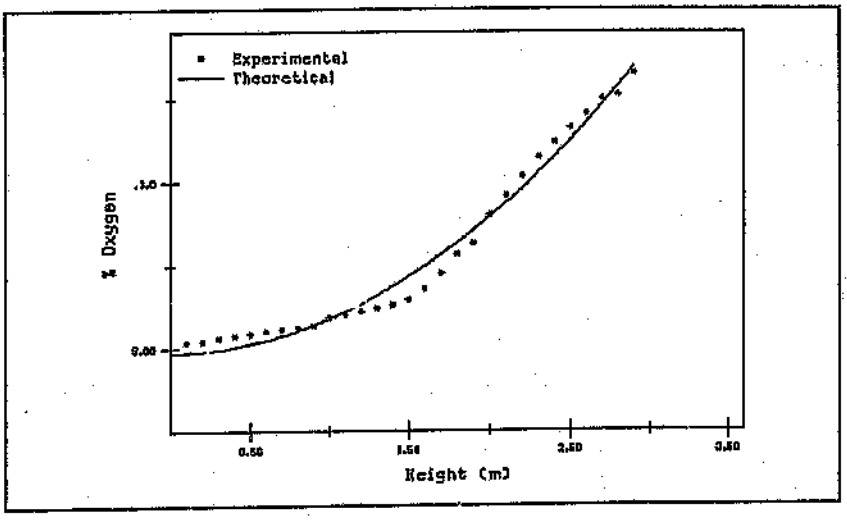


Fig.A.3.6 Fitting for oxygen profile for December 1995

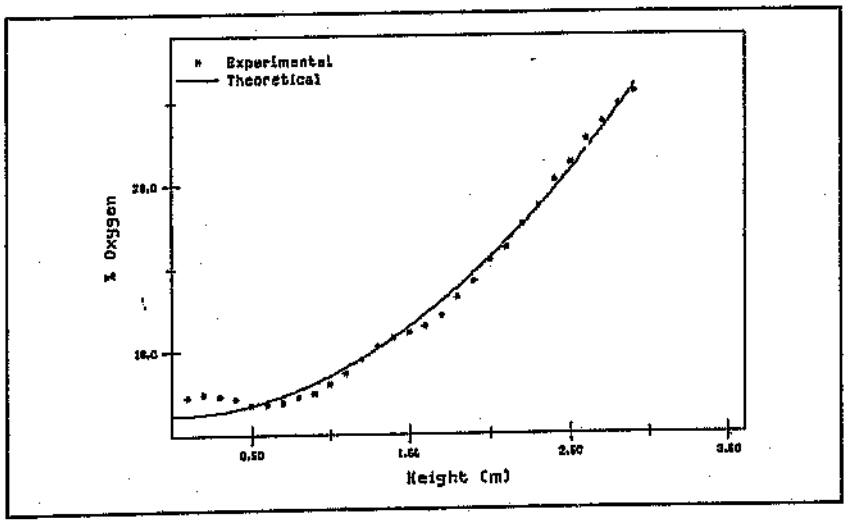


Fig.A:3.7 Fitting for the oxygen profile for March 1996

Appendix B

Calculations of the isothermal oxidation experiments

The equations given below were used for calculations for experimental measurements described in section for the isothermal low temperature oxidation.

For the corrected height h which is also assumed to be equal to the volume (ml) of the oxygen absorbed:

1) $h = (h_{o\,cool} - h_{i\,cool}) - (h_{o\,blank} - h_{i\,blank})$

where: $h_{o\,cool}$ is initial height of oil in sample.

$h_{i\,cool}$ is height of sample at any given time.

$h_{o\,blank}$ is initial height of the blank.

$h_{i\,blank}$ is height of blank at any time (t).

2) $n_{o2\,flask} = 0.21*(PV/RT)$

where: $n_{o2\,flask}$ = is initial number of moles of oxygen in the flask.

P is the ambient pressure.

T is the initial temperature.

V is the volume of the apparatus.

R is the gas constant

3) $n_i = PV_i/(R*(273 + T_i))$

where: n_i is number of moles of oxygen at any given time.

V_i is the volume of oxygen absorbed at the given time.

T_i is the temperature at any given time (t).

4) $n_{i\,flask} = (n_{o2} = n_i)$

5) $[O_2] = n_{o2} - n_i/V_o - V_i$

where:

V_o is the initial apparatus volume

V_i is the volume of the apparatus at any given time.

Calculation for Air flow rate

A flow meter FP -1/16 - 12 - G-5 using a sapphire float was used to determine the flow rate of the air.

The equation is given as:

$$W = CB\sqrt{(\rho_f - \rho_{opt})\rho_{opt}}$$

$$N = \frac{A}{\mu_{opt}}\sqrt{(\rho_f - \rho_{opt})\rho_{opt}}$$

$$\mu_{opt} = \mu_{st} + (Temp\ coefficient)(t - 70)$$

Where: W is gravimetric flow rate (g/min)

C is flow coefficient

A is size factor

U_{OPT} is fluid viscosity at OPT

centipoise

p_f is float density g/cc

p_{OPT} fluid density at OPT

B is

$$W = 0.218 \times 13.6\sqrt{(3.98 - 0.0060023) \times 0.0060023}$$

$$W = 0.457897 g/min$$

$$W = 380 cc/min$$

Given below is the numerical data of the graphs given in section 4 of the dissertation.

10% oxygen concentration

time (min)	moles of oxygen absorbed
0	0
12	7.1E-05
12	7.1E-05
16	7.1E-05
16	7.1E-05
19	1.1E-05
20	1.1E-05
20	1.1E-05
32	1.8E-05
32	1.8E-05
36	1.8E-05
36	2.1E-05
40	2.2E-05
40	2.5E-05
60	2.9E-05
60	2.9E-05
63	3.2E-05
63	3.2E-05
72	3.2E-05
72	3.2E-05
83	3.6E-05
107	3.9E-05
107	3.9E-05
110	3.9E-05
110	4.6E-05
113	4.6E-05
130	5.0E-05
130	5.0E-05

continued overleaf...

time (min)	moles of oxygen absorbed
137	5.4E-05
137	6.1E-05
154	6.4E-05
154	6.4E-05
158	7.1E-05
178	7.5E-05
178	7.8E-05
178	7.8E-05
182	7.9E-05
202	8.2E-05
202	8.9E-05
206	9.6E-05
206	

21% Oxygen concentration

time (min)	moles of oxygen absorbed
20	2.13E-05
20	3.19E-05
24	2.47E-05
24	3.19E-05
28	3.1E-05
28	3.55E-05
44	6.38E-05
44	6.74E-05
48	6.38E-05
48	7.09E-05
52	6.74E-05
52	7.45E-05
68	7.09E-05
72	7.8E-05
72	8.51E-05
76	7.45E-05
76	7.8E-05

continued overleaf...

time (min)	moles of oxygen absorbed
92	1.03E-04
92	1.06E-04
96	1.6E-04
96	1.1E-06
100	9.93E-04
100	1.03E-04
116	1.38E-04
116	1.42E-04
120	1.42E-04
120	1.45E-04
124	1.21E-04
124	1.24E-04
140	1.6E-04
140	1.63E-04
144	1.63E-04
144	163E
148	1.67E-04
164	1.88E-04
164	1.92E-04
172	1.88E-04
172	1.88E-04
188	2.2E-04
188	2.23E-04
196	2.16E-04
196	2.2E-04
212	2.41E-04
212	2.48E-04
220	2.34E-04
220	2.34E-04
244	2.52E-04
244	2.48E-04
260	2.8E-04
260	2.8E-04
268	2.7E-04

continued overleaf...

time (min)	moles of oxygen absorbed
268	2.66E-04
284	3.05E-05
284	2.73E-04
292	2.98E-04
292	2.84E-04
306	3.19E-04
306	2.98E-04
316	3.05E-04
330	326E-04

50% Oxygen concentration

time (hrs)	moles of oxygen absorbed
0	5.0E-05
12	6.1E-05
12	7.1E-05
16	9.0E-05
20	1.0E-04
20	1.5E-04
20	1.6E-04
28	1.6E-04
28	1.9E-04
28	1.8E-04
32	1.9E-04
32	2.1E-04
32	2.0E-04
40	2.5E-04
40	2.7E-04
40	2.9E-04
72	3.0E-04
72	3.3E-04
72	3.9E-04

99% Oxygen concentration

time (hrs)	moles of oxygen absorbed
0	0
12	1.2e-04
12	1.3E-04
12	1.4E-04
16	1.5E-04
16	1.7E-04
16	2.0E-04
20	2.4E-04
20	2.5E-04
20	2.7E-04
28	4.04E-04
28	4.10E-4
32	4.4E-04
32	4.5E-04
40	4.8E-04
40	5.0E-04
72	6.8E-04
72	7.1E-04

Appendix C

Drying experimental data.

Run 6

time (hrs)	mass of moisture (g)
0	15.86
2	13.96
3	12.69
8	11.42
24	7.61
27	6.35
32	5.71
48	5.71
51	3.81
55	3.81
72	3.17
79	1.90
99	1.27
103	0
120	0

Run 7

time (hrs)	mass of moisture (g)
0	14.38
2	13.28
3	13.28
8	11.06
24	4.43
27	3.87
48	3.32
51	2.21
55	1.66
72	1.11
79	0.55
99	0.55
103	0
120	0

Run 8

time (hrs)	mass of moisture (g)
0	16.90
2	15.65
13	12.52
24	6.89
27	6.26
32	6.25
51	3.13
72	2.50
79	1.25
99	1.25
103	0
120	0

Run 9

time (hrs)	mass of moisture (g)
0	17.70
2	12.78
3	12.29
8	8.85
24	7.86
27	7.87
32	4.92
48	2.46
51	2.46
72	1.47
79	0.98
99	0
120	0

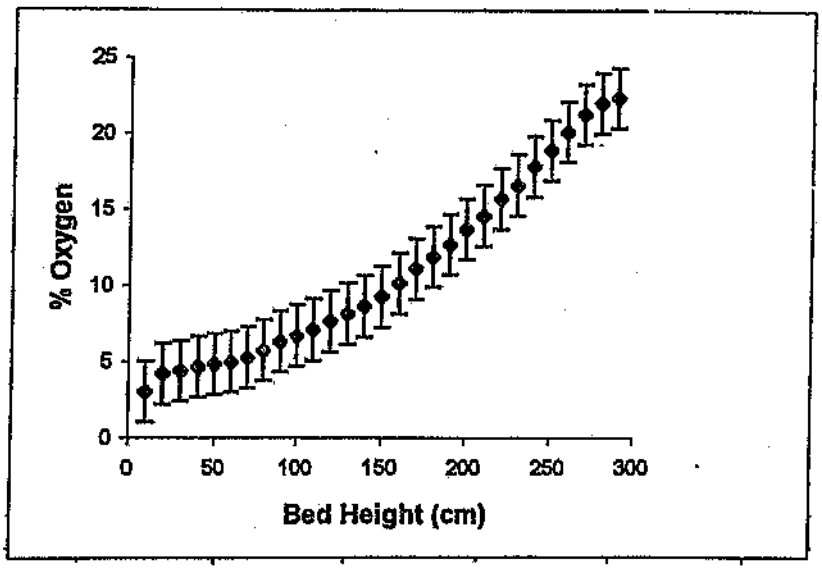
Run 13

time (hrs)	mass of moisure (g)
0	17.79
2	15.56
4	12.23
8	11.11
24	5.56
26	5.56
32	1.11
52	1.11
72	0
95	0

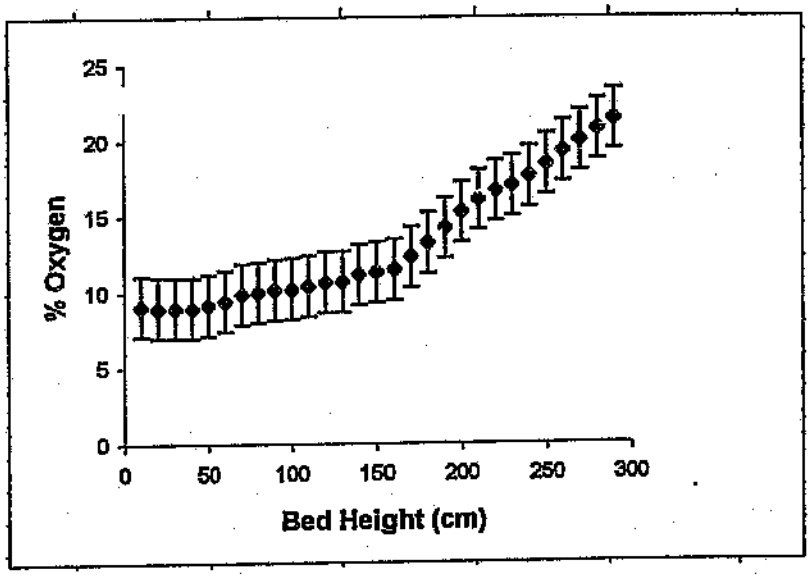
Error Analysis

Errors are not mistakes, one cannot avoid them by say being very careful. The best one can hope for is to ensure that errors are as small as possible, it is also important to have some reliable estimates on how large they are.

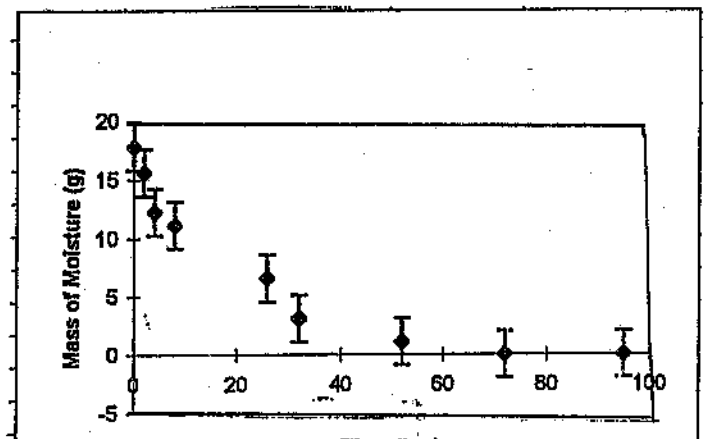
One has to evaluate the magnitude of uncertainty, there are simple measurements for which it is easy to make reasonable estimates of uncertainty. For the pipe reactor and the drying experiments graphs below show the uncertainties in % oxygen and mass of moist re.



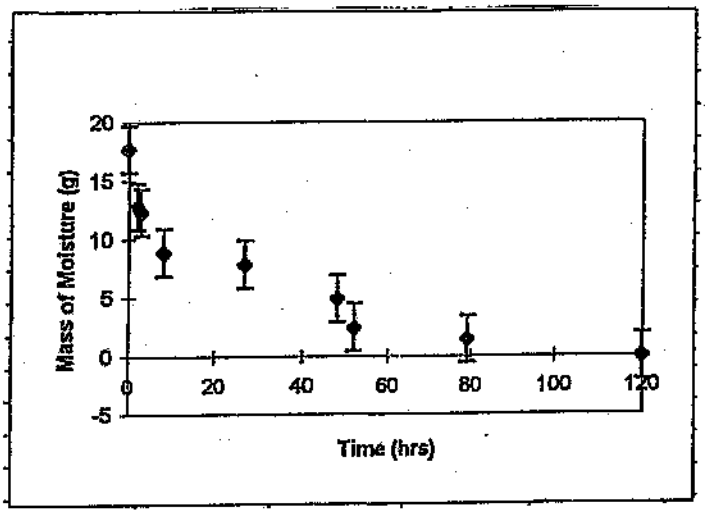
February results run 1



January results run 2



Drying run 13



Drying run 9

Error introduced by the static head of the column of the oil sucked up should be very negligible, this is mainly because column height is very low which in turn makes the partial pressure effect very minimal.The pressure of the oxygen absorbed was found to be about 4 millibars.

Reliability Factor R^2

The reliability factor is used to assess how reliable results are and can also be used to compare fits of different models describing the same data. If the data fits the model well R^2, the reliability factor should

approach unity. For results in chapters 3 and 5 excel was used to calculate the r iability factor and fairly reasonable to very good fits were found. Given below are the results of the drying experiments.

Run	R-Squared value
6	0.9776
7	0.8664
8	0.9591
9	0.9169
13	0.7859

For the oxidation experiments R^2 values ranging from 0.6859 to 0.9645 were obtained, this also a general acceptance of the fit of the experimental data to the model.